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A small-sized DSSC panel based on the Uruguayan national flower dye tested at the Antarctic Artigas Base

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Abstract. The construction of a small-sized panel based on anthocyanins from *Erythrina crista-galli* as sensitizers is reported in this work. The device, named KD12, was placed indoors at the Artigas Antarctic Scientific Base from March 2019 to December 2020. Here is released for the first time, the indoor installation of dye-sensitized solar cells based on pigments from the Uruguayan national flower at an Antarctic Base and the evaluation of their performance during nineteen months. The panel showed good stability and maintained its efficiency conversion performance over the period. The output power, voltage and conversion efficiency generated for this device mainly depended on irradiance and external factors as light reflection due to snow or artificial bulbs near the area. Additional protection was provided by the double-glass window in front of the panel, lowering lighting irradiance and changing spectral characteristics of the light incident the device. A new prospect raised here: the potential application of anthocyanins as sensitizers for indoor electricity generation in the Antarctic area with long term operability, where low temperatures are helpful considering the thermal stability of the dyes. These constitute an interesting first step of a low-cost alternative searching for clean energy generation sources, focusing on a cold region like Antarctica.

Keywords: Anthocyanins / *Erythrina crista-galli* / dye-sensitized solar cell

1 Introduction

The search for new strategies for obtaining energy constitutes an actual concern. Many approaches involve using renewable, but the application of Solar is lagging in comparison with other sources and remains still underutilized. Economic factors also play a role, and investing in new ways of energy conversion also requires many answers [1–3]. At present, the use of solar modules has become economically viable and competitive with fossil-fired electricity. Particularly, attention is turning to explore new uses and approaches such as designing and characterizing specific modules for indoor applications.

Dye-sensitized solar cells are widely reported as an alternative option for photovoltaics [4–6]. Mentioned for the first time in 1991 [7], they have experienced an increasing interest from the initial possibility of converting the light into electricity to the application in BIPV and greenhouses [8–11]. The reported applications are exclusively based on the use of synthesized ruthenium dyes. Assembled in large panels and integrated into the buildings, Lausanne's Swiss Convention Centre constitutes one of the most remarkable examples of such technology [12].

Concerning the search and use of natural dyes in DSSC, reports in the literature are abundant [13–17]. Unfortunately, two significant disadvantages arise among many benefits: low conversion efficiencies and lack of stability. However, DSSC still offers two huge advantages: they remain functional even under diffuse light and are transparent to be used as power-generating building blocks [8]. And recently, efforts devoted to designing and optimising specific DSSC modules for indoor applications have been reported [18–20].

They can also provide an exciting alternative to profit large amounts of natural waste: dyes extracted from fallen flowers that wither, fruits' peels, leaves from felled trees for paper pulp production, or even invasive seaweeds could find an alternative to be exploited. Pigment extraction from these sources could be as easy as using a suitable solvent [21–23]. And still considering the low efficiency for the assembled cells, providing an application for tons of unutilized biomass deserves to be considered.

Then, the assembly of DSSC-modules using natural dyes constitutes an exciting and unexplored goal: cheap and environmental-friendly since pigment extraction is effortless and involves non-harmful reagents and methods. The evaluation of these devices' stability and performance with time is still a pending question to solve. In this sense, the present report intends to contribute to the field and

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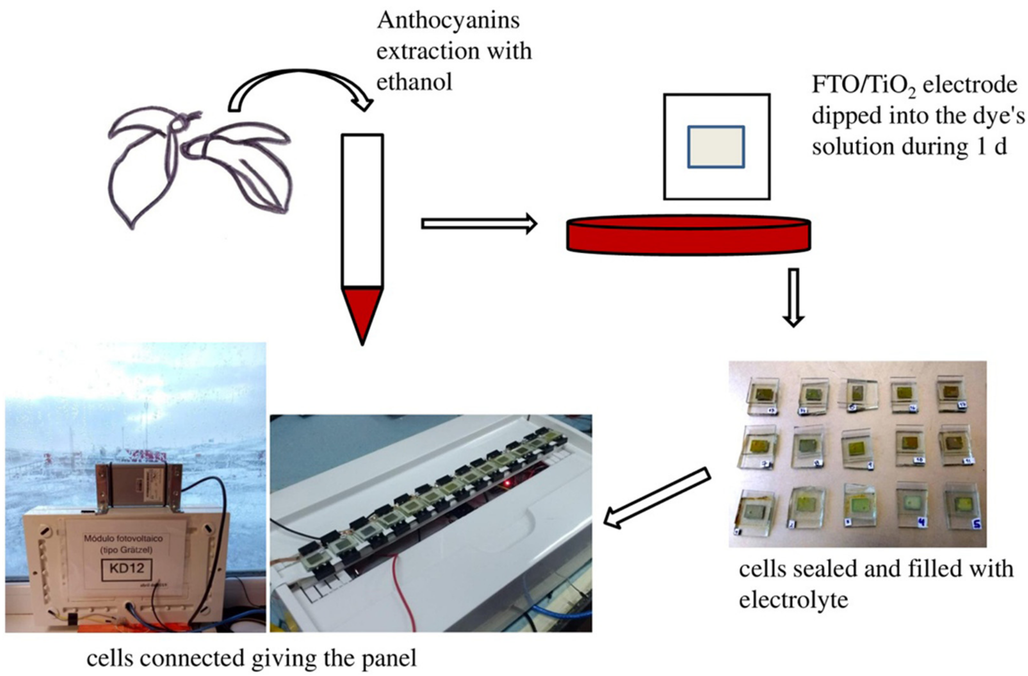

Sch. 1. Representation of the individual cells' assembly and further connection to the small-sized panel.

place a question: could be used unutilized natural waste to produce energy, at least in cold areas? Regions as Antarctica offer a gold opportunity to evaluate new applications for DSSC. As discussed, these modules can be placed in the windows or even inside the buildings: protection against climate inclemency is then assured. And if sensitizers are natural dyes, the low temperatures constitute an ally regarding thermal stability.

Here, we reported the power data generated from a small-sized panel made from cells sensitized with anthocyanins extracted from Uruguay's National flower: *Erythrina crista-galli.* The device, called KD12, was placed at the Artigas Antarctic Scientific Base (King George Island/Isla 25 de mayo) from March 2019 to December 2020. Data were remotely monitored and processed at Montevideo, with promissory results.

2 Materials and methods

2.1 Anthocyanins' extraction

The "ceibo" flowers were cut into pieces and immersed in 95% ethanol to extract the anthocyanins [24]. The resulting solution was then centrifuged to remove the solids and purified using a C18 disposable column (BAKERBOND spe^{TM}, octadecyl C18) with methanol-acetonitrile (30/70) mixture as an elution solvent, to eliminate the chlorophyll. The eluted solution was concentrated under nitrogen and re-dissolved using ethanol.

2.2 Cells' assembly

Each cell contains a photoanode of FTO/TiO_2 (DYESOL, screen printed with Dyesol's DSL 18NR-AO Active Opaque Titania paste, 0.7 cm^2) and an FTO/Pt (screen printed with SOLARONIX's Pt Platinum Catalyst) as the counter electrode. The photoanodes were preheated at 500 °C for 30 min. After cooling at room temperature, they were sensitized with anthocyanins extracted as described above, dipping the FTO/TiO_2 electrode overnight into the dye's solution. This step is crucial to assure the adsorption of anthocyanins molecules onto the TiO_2 surface.

To assembly the cells, a sandwich configuration was adopted. The space between electrodes was then filled with an electrolyte and sealed with a gasket. The selected electrolyte was 50 mM iodide/tri-iodide in acetonitrile (SOLARONIX Iodolyte AN-50). Cells were sealed with a hot-melt gasket of 25 μm thickness made of the ionomer Surlyn 1702 (Dupont) using a laboratory heating plate at about 110 °C [25].

The cells' assembly procedure and the connection of the individual cells to the small-sized panel are represented in Scheme 1.

The individual cells were evaluated after being mounted. Current density vs voltage (J–V) measurements performed with a CHI 604E potentiostat allowed the evaluation of the cells' conversion efficiency. J–V characterizations were accomplished at a potential scan rate of 0.05 V s^{-1} (at room temperature, under illumination using a solar simulator from ABET Technologies, 1000 Wm^{-2}, 1.5 AM).

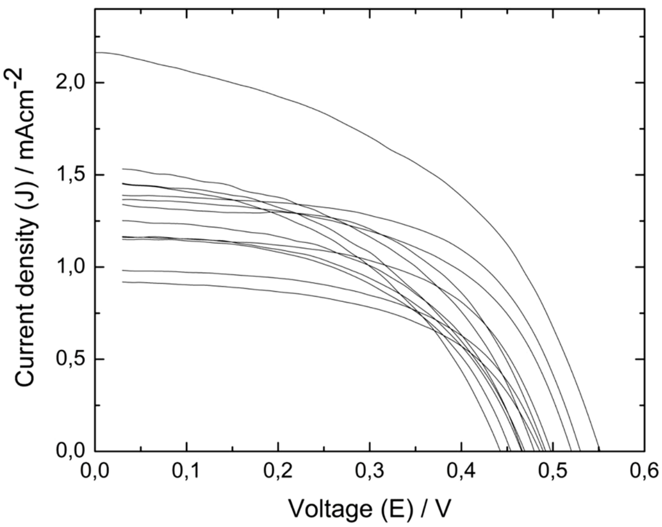

Fig. 1. Current density vs potential profiles for all the cells assembled in the DSSC panel.

2.3 Panel construction and characterization

The module named KD12 comprises thirteen individual cells connected in parallel (with a total area of 9.1 cm^2), chosen accordingly to their conversion efficiency values among many prepared. Connections were made using copper ribbons and office clips.

KD12 was placed inside one of the buildings of the Artigas Antarctic Scientific Base King George Island/Isla 25 de mayo, 62°11′04″ S – 58°51′07″ W), in front of a window (oriented to the Northwest, vertical orientation parallel to the window, as shown in Sch. 1).

KD12 was connected to an Arduino board, monitoring the generated data remotely through collection in the cloud with advanced analysis using MATLAB Analytics with the ThingSpeak platform for IoT Projects [26]. The measured voltage was displayed in channel 2, whereas channel 1 collected voltage data measured from a circuit including a 5.5 kΩ resistance connected to the Arduino board.

For comparison purposes, a Solar Irradiance Sensor (SIS, Ingenieurbüro, Mencke & Tegtmeyer GmbH) was installed indoors on top of the dye-sensitized panel (Sch. 1). The SIS is a photovoltaic reference cell made of monocrystalline silicon (5.0 cm × 3.3 cm) connected to a low resistance shunt.

Irradiance mean values at 45° were obtained from a pyranometer placed at the top of one of the buildings of the Artigas Base. MIEM-DNE (Dirección Nacional de Energía, Uruguay) provided the irradiance data.

2.4 Data processing

Data were processed using Origin (Pro) 7.0 (Version 2002, OriginLab Corporation, Northampton, USA).

Data generated from KD12 were logged each minute and processed to calculate its corresponding power value. The evaluated period ranges from March 1st. 2019 to December 7th, 2020. We remotely processed the generated data, obtaining them through the Antarctic Base's Wi-Fi connection. Therefore, the lacks of them are due to connection failures. Some punctual experiments were added, performed during June 2021 at Montevideo, Uruguay.

Table 1. Mean irradiance measured at a tilt angle of 45°, along the evaluated period. Mean and SD values were calculated from the five highest values of each month.

Month	Mean irradiance/Wm^{-2}	± SD
May 19	132	35
June 19	43	10
July 19	77	11
Aug. 19	199	14
Sept. 19	426	23
Oct. 19	627	27
Nov. 19	835	19
Dec. 19	875	29
Jan. 20	827	57
Feb. 20	646	32
Mar. 20	537	10
Apr. 20	287	22
May 20	134	16
June 20	44	3
July 20	108	29
Aug. 20	290	41
Sep. 20	465	28
Oct. 20	701	26
Nov. 20	745	36

As previously mentioned, channel 2 displayed the generated voltage of KD12 and channel 1, the voltage measured from a circuit including a 5.5 kΩ resistance. The current was estimated using Ohm's expression from the measured voltage values displayed on channel 1, considering the resistance. By multiplying the values from channel 2 and the intensity from channel 1, it was possible to calculate the output powers. The power conversion efficiencies (PCE) were calculated from the ratio between these estimated power outputs to the incident irradiance.

It is important to remark that Arduino boards are able to read analogue inputs. They are designed to measure DC voltage between 0 and 5 V. Consequently, it is necessary to include a resistor connected to the board when the current intensity needs to be estimated.

Besides, channel 3 registered the voltage generated by the SIS unit.

3 Results and discussion

3.1 Individual cells' characterization

Before being connected and assembled to build the panel, we evaluated the individual cells' performance. From profiles displayed in Figure 1, calculated conversion efficiencies for the utilized cells ranged between 0.24 and 0.55%, with a mean value of 0.44 ± 0.2%. These calculated

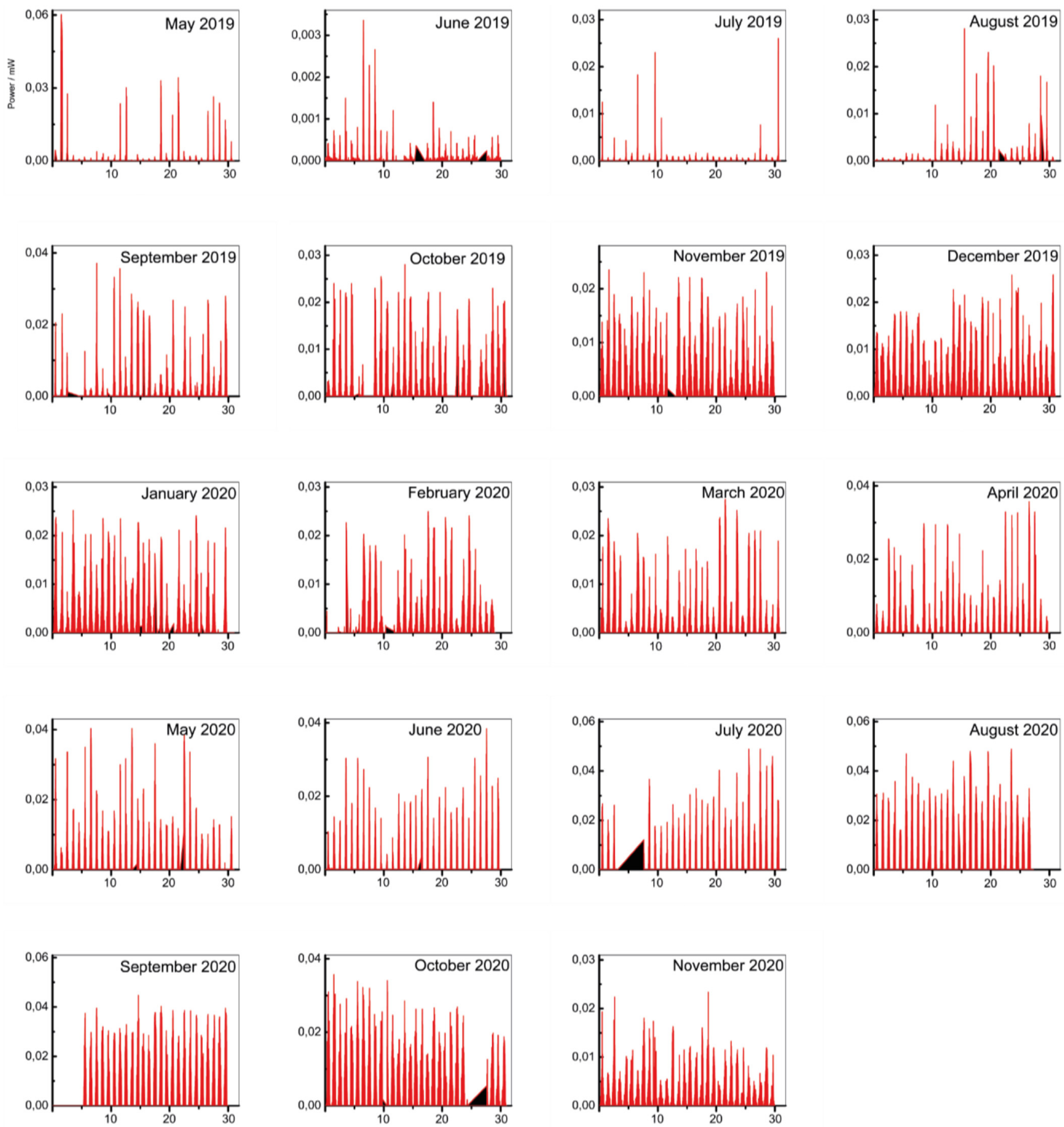

Fig. 2. The daily performance's for the DSSC-panel KD12 along the whole period of the test. The module was placed in front of a window inside one of the Artigas Antarctic Base buildings.

values were obtained from the measured profiles under controlled illumination conditions (1000 $\mathrm{Wm^{-2}}$). A potentiostat was used to get current intensities (and with the electrode area, current densities) and voltage values.

The results were lower than those previously reported for open cells (ca. 0.7%) based on the same dye, and the standard deviation was ten times higher [24]. Cells were sealed using a heating plate at 110 °C, and this procedure affected dye degradation. The influences of this step on the cells' efficiency and, therefore, on the panel's outputs have to be considered.

Nevertheless, once assembled, individual cells' efficiency values remained unchanged under the same laboratory evaluation conditions and were selected to build the panel.

Table 2. Mean power, mean maximum voltage and mean power conversion efficiency generated by KD12 along the evaluated period. Mean and SD values were calculated from the six highest values of each month.

Month	Mean Power mW	SD	Maximum voltage V	SD	PCE %	SD
May 19	0.035	0.012	0.56	0.02	0.030	0.002
June 19	0.0021	0.0009	0.19	0.03	0.0054	0.0001
July 19	0.016	0.007	0.47	0.05	0.0228	0.0004
Aug. 19	0.021	0.004	0.51	0.03	0.0116	0.0003
Sept. 19	0.032	0.004	0.54	0.02	0.0083	0.0005
Oct. 19	0.025	0.002	0.57	0.01	0.0044	0.0003
Nov. 19	0.023	0.001	0.510	0.007	0.0031	0.0001
Dec. 19	0.024	0.002	0.49	0.01	0.0031	0.0003
Jan. 20	0.024	0.001	0.468	0.007	0.0032	0.0003
Feb. 20	0.023	0.001	0.46	0.02	0.0039	0.0002
Mar. 20	0.024	0.003	0.46	0.02	0.0049	0.0001
Apr. 20	0.033	0.002	0.496	0.005	0.0127	0.0002
May 20	0.037	0.003	0.515	0.003	0.0304	0.0002
June 20	0.031	0.004	0.48	0.01	0.0774	0.0001
July 20	0.045	0.004	0.52	0.02	0.0462	0.0006
Aug. 20	0.046	0.004	0.53	0.01	0.0174	0.0008
Sep. 20	0.041	0.002	0.52	0.02	0.0097	0.0003
Oct. 20	0.025	0.005	0.513	0.006	0.0039	0.0006
Nov. 20	0.020	0.003	0.46	0.01	0.0030	0.0005

3.2 Climatic characterization

For comparison purposes, weather data were taken into account for the nineteen months of monitoring, focusing on irradiance availability and ambient temperature trends.

The average temperatures at the Island ranged around −2 °C and −16 °C, for the hottest and coldest months [27]. From the beginning of January to the end of February, days showed a mean maximum temperature of −3 °C, with a mean minimum of −5 °C. The mean maximum temperature between June and August was −8 °C, with a mean minimum of −16 °C.

Irradiance values varied during the day and month of the year (Tab. 1). As expected, irradiance showed their maximum values from December to February and minimal in June/July.

3.3 Indoor performance on a sunny day

As a first step, we evaluated the DSSC module's daily performance.

Radiation during the evaluation period varied and was monitored as mentioned in Section 2.3. Once again, it is essential to remember that the dye-sensitized panel was located inside, in front of a double-glass window. Then, the indoor light intensity received by the device is lower than sunlight, and the spectra also differ considerably [19]. Also, it is important to mention the existence of poles with artificial light bulbs installed near the window where KD12 was placed. And, in snowing periods, snow has accumulated in front of the window without covering the opening completely. But, on those days, the DSSC-panel was protected from the inclement weather inside the building.

Thus, data analysis is described in terms of highlighting the unique characteristics of DSSCs integrated inside a building; specifically, the long-term operability of a DSSC panel based on a natural pigment in the Antarctic base.

3.4 Stability and performance

Figure 2 shows all calculated power (in mW) from each measured minute, graphically displayed as a time function. Output powers vary during the day and the months following the light radiation intensity changes.

Analysis of the data is simplified using some selected numeric records. Table 2 shows the mean power values and the sample standard deviation calculated selecting the six higher powers generated each day. Also, the mean values of maximum voltages and the power conversion efficiencies (PCE) values are included in Table 2.

PCE are lower than those calculated for the individual cells. The explanation is simple: they are incomparable. The evaluation conditions were different. On one side, it has to be remembered that the current intensity, then the power, and consequently the PCE of the panel are estimated from a circuit including a high resistance of 5.5 kΩ from Arduino's voltage data. While individual cells efficiencies were calculated from current densities vs voltage profiles using a potentiostat. In addition, cells were joined using standard office connectors without considering the resistances added to the whole electric circuit: other contributions to loss in power

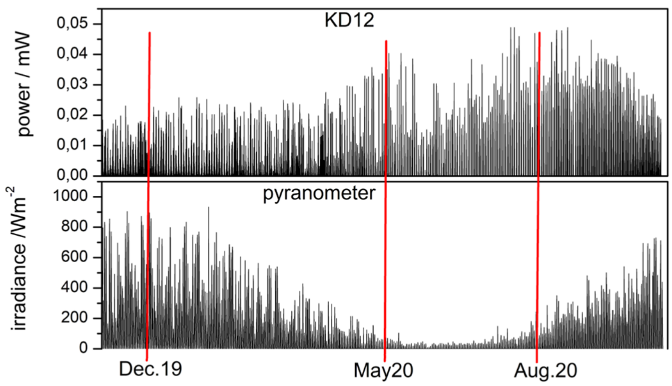

Fig. 3. Irradiance measured by a pyranometer and estimated power for the DSSC panel from November 2019 to November 2020.

conversion efficiencies. And also, the incident light is different for individual cells (tested at standard test conditions using a solar simulator under controlled irradiance, i.e. $1000\,\mathrm{W\,m^{-2}}$ average irradiation, with AM1.5G spectral coefficient and a temperature of 25 °C) and for the KD12 panel (according to Tab. 1 the mean irradiance at Antarctica was variable and lower than $1000\,\mathrm{W\,m^{-2}}$ during the evaluation period). Once again, it has to be considered that KD12 was placed next to a window, where glasses are affecting irradiance and spectra of the incident light. Table 1 displays outdoor solar irradiances measured, but no values of the indoor lighting (undoubtedly lower) experimental conditions are available. The performance PCE varies and responds to different parameters in varying operating conditions. At the same illuminance, different light spectra will produce different irradiance.

In short: displayed individual cells efficiencies are the highest and the displayed PCE of the panel are only an estimation and not coincident with the maxima outputs.

Regardless of the low calculated numbers, some interesting points and tendencies arose and are discussed below.

Tendencies are in line with at least two factors: solar irradiance and other external elements as, probably, the presence of snow. From December to March, irradiance increases, and the opposite occurs during June to September. Nevertheless, power and mean voltage values did not decrease dramatically during the latter period.

The lack of adjusting between KD12's generated power and irradiance is evidenced by tendencies shown in Figure 3.

An alignment between power output values and irradiance is expected: power increases as irradiance increases. From May to August, irradiance reached a minimum. However, the dye-sensitized KD12 device generation was almost the same during this evaluation period.

Clearly, irradiance shows a significant dependency on the duration of the day and the Sun inclination. From June to September, irradiance is much lower than in other months. Contrary to irradiance tendencies, generated power by KD12 did not follow the same path.

When PCE values are analyzed, there is something still more notorious: June '19 is the lowest, as expected, but the mean value of June '20 is one of the highest ones.

External factors have to be taken into account, and the presence of snow and artificial light next to the window where KD12 is placed are two of them. We briefly evaluated these two aspects, as discussed below.

Initially, we tested the dye-sensitized panel during some days at the Antarctic Base. The device showed an exciting dependence on outdoor artificial lighting placed near the window. After this initial trial, the panel was installed and connected to the Wi-Fi.

Something similar happened on snowy days: the snow's reflection of light near the window also increased the dye-sensitized panel's power generation.

We also performed some measurements at Montevideo during June 2021 (average temperature of 10 °C), emphasizing the role of snow. We are aware that climatic conditions for Montevideo in winter are far from those at the Artigas Antarctic Base. And one point has no discussion: there is no snow in this city in winter. Placed close to a glass window, the KD12 panel under an irradiance of $59 \pm 15\ \mathrm{Wm^{-2}}$ (natural light) generated an output mean power of $0.005 \pm 0.001\,\mathrm{mW}$ (with maximum voltage $0.203 \pm 0.020\,\mathrm{V}$).

A small area monocrystalline silicon sensor placed at the top of the KD12 was also monitored for comparison purposes. No response was measured when this device of 15 $\mathrm{cm^2}$ was lighted with the light from an artificial external pole near the window, while the opposite occurs with the DSSC, as previously tested at the Antarctic Base. The explanation depends on some factors. Ambient indoor light intensity is smaller than sunlight, especially from an outside source near the window where devices were installed. And the spectra between these light sources vary considerably. Moreover, crystalline silicon is designed for outdoor installations with a spectral sensitivity that matches natural sunlight, while dye-sensitized cells are better candidates for indoor application [18,19].

It is also interesting to analyze the different behaviour of the DSSC and the silicon-photovoltaic placed together indoors. As observed in Table 3 and Figure 4, the small silicon photovoltaic reference could generate voltage values (recorded in channel 3) when incident irradiance exceeded an irradiance value of $100\,\mathrm{W\,m^{-2}}$. Table 3 shows selected values displayed at the three channels of the Arduino board, which illustrate the different responses of the dye-sensitized and the monocrystalline cells to the incident light. Also, the data coming from channel 3 during the experimental period is shown in Figure 4.

Results can be explored in more detail, considering Figure 5 and Tables 1 and 2. For similar irradiance values (October and December 2019), the mean generated power by KD12 and the PCE were almost the same – nevertheless, the maxima voltage were not. Irradiance could have a more significant influence on intensity values than on generated voltage. The power and PCE produced in August 2020, among the highest averages, when irradiance was lower than in October 2019, also pointed to support this statement.

Table 3. Some examples of the measured voltage of the Solar Irradiance Sensor (SIS) installed close to the DSSC panel, with the corresponding irradiance values for those data. Registered data for KD12 are also included for comparison purposes.

Date	time	SIS measured voltage (V)	Irradiance ($\mathrm{W\,m^{-2}}$)	KD12 measured voltage (V)	
				Channel 1	Channel 2
22/5/19	13:17	0.03	110	0.27	0.52
31/7/19	13:29	0.03	100	0.16	0.4
20/08/19	14:41	0.02	158	0.2	0.47
8/09/19	13:58	0.05	259	0.31	0.52
14/10/19	13:01	0.05	522	0.23	0.45
8/03/20	15:23	0.05	481	0.21	0.35
14/04/20	13:43	0.03	199	0.19	0.43

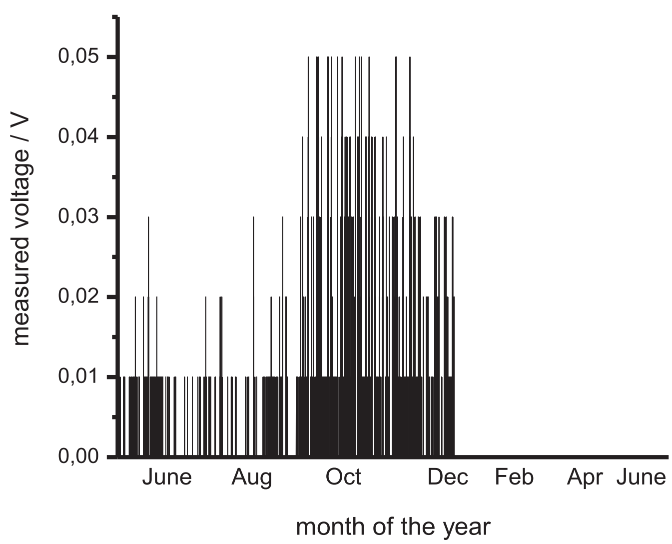

Fig. 4. Voltage values recorded at channel 3 for the Solar Irradiance Sensor (SIS) installed close to the DSSC panel during the measurement period.

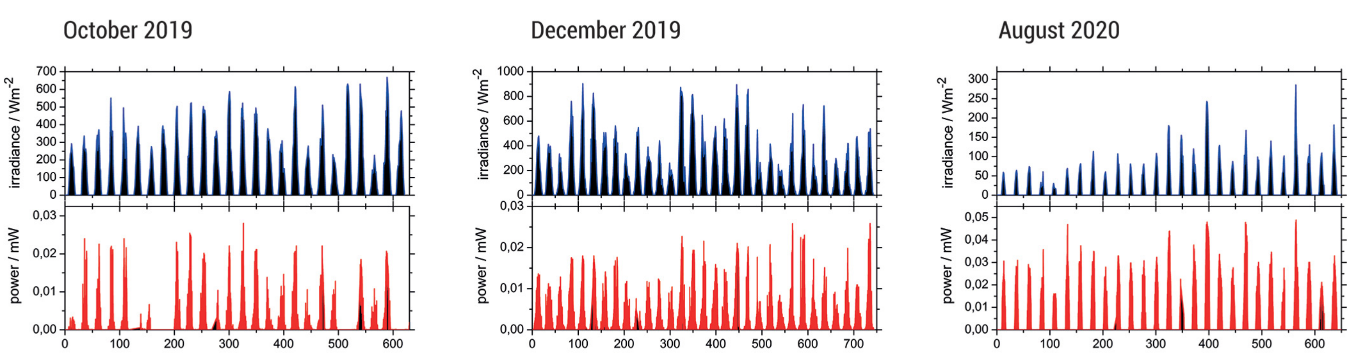

Fig. 5. Irradiance measured by a pyranometer and calculated power for the DSSC-panel during some specific months.

As stated above, we cannot neglect the influence of some particular external factors as the presence of snow. The year 2019 was exceptional, with low averages snowfalls compared to other years, and 2020 in particular. The snow could explain the results displayed in Figure 5, especially the poor records of June 2019.

Let us look more detailed at data generated in June 2019 for the DSSC. The small dye-sensitized device generates every day, even when irradiance values are too low. Inherent characteristics could be the explanation stressing the unique characteristics of DSSC when integrated inside a building. The DSSC-based panel could show a more remarkable ability to profit from other light sources in the area, as reflected and artificial light.

The representation of the power output from a photovoltaic panel vs. voltage increases until it reaches a maximum; each device has its characteristics. In the case of our dye-sensitized array, the here reported power values are an estimation. As mentioned, output powers were calculated using the Ohm's expression from the measured voltage values obtained with a 5.5 kΩ resistance connected to an Arduino board. Then, and as stressed previously, KD12 power values are not precisely the maximum output ones, especially considering the differences between the voltages displayed at channels 1 and 2 and the expected tendencies for reported standard P-V curves for DSSC [28,29].

Nevertheless, it is possible to arrive at some conclusions from the observed tendencies and values exposed above.

The panel assembled from anthocyanins' sensitized cells could generate power and voltage with a maintained efficiency conversion performance during the evaluation time. These constitute essential points since stability is a crucial point to be considered for cells based on natural dyes. The DSSC panel can profit from other additional light sources from the surrounding area, such as snow's reflected light.

Once again, the presence of the double-glass window in front of the panel must be considered. Glass blocks UV radiation, mainly UVB rays, protecting DSSC from failures due to electrolyte bleaching or to natural dyes degradation as reported [30,31]. Also, lower indoor lighting irradiance would explain the good stability of the anthocyanins based panel over the nineteen testing period.

The results presented here showed the potential application of anthocyanins extracted from the Uruguayan national flower as sensitizers for indoor electricity generation in the Antarctic area with long term operability. Here, the low temperature also contributes to the thermal stability of the dyes. Calculated power is improved by external factors commonly present nearby the Antarctic Bases' buildings where DSSC can be placed, like light bulbs and reflected light due to snow.

Thus, photovoltaic cells sensitized with natural pigments appear to be strong candidates for indoor applications, and the results presented in this work offer answers to certain aspects of their use in cold regions, with no previous studies yet reported.

4 Conclusions

The use of DSSC technology is an attractive alternative to explore in cold regions with possible energy production for modules located inside buildings; therefore, protected from snow and bad weather conditions.

Despite the low conversion efficiency compared to synthetic dyes, the easy and inexpensive fabrication steps based on natural dyes make anthocyanin-based DSSCs an exciting solution to evaluate. They can also provide a compelling alternative for taking advantage of large amounts of natural waste by extracting natural dyes from fallen flowers that wither away, fruits' peels, leaves from felled trees for paper pulp production, or even invasive algae.

Two significant achievements have been reported here for the first time: the use of natural dye sensitized cells in an Antarctic base and the construction and evaluation of a DSSCs module over a period of nineteen months. This module showed good stability and maintained conversion efficiency performance over time in indoor conditions.

Placed in front of a double-glass window, the small-sized panel based on anthocyanins from *Erythrina crista-galli* showed output power, voltage and conversion efficiency mainly depended on irradiance and external factors as light reflection due to snow or artificial sources near the area.

The results informed here constitutes an interesting first step of a low-cost alternative searching for clean energy generation sources with a particular focus in a cold region as Antarctica. The decrease in the use of fossil fuels and derivatives is a priority target to achieve in Antarctica. Then, exploration of materials for renewable energy storage and conversion, mainly based on natural resources, could provide a partial solution. The exploitation of solar is sub explored in that area, where, for instance, dye-sensitized solar cells can be installed indoors with good functioning capacity.

Improvement of efficiency represents a great starting point for future research.

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