MICROGENERATION OF ENERGY WITH ELECTROLYTE USE ORGANIC SUBSTRATE COMPOUNDS

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ABSTRACT

The search for energy sources is something inherent in the history of society and even more so with the impact of industrial revolutions, which have forced a growth in the use of fossil fuels. Oil crises and environmental treaties led to the deepening of research and applications in Renewable Energies. Among these several kinds of research, the development of electrochemical cells stands out. These cells may have chemical and biochemical reactions. This range of information often generates technical doubts for its applications in the design of electrical and electronic products, which seek to reduce its impact, mainly in the final disposal. In this sense, the present research seeks to contribute with technical-scientific data guiding for the generation of micro-energy, from the use of natural materials to manufacture the biochemical cell. In view of this requirement, ten natural materials with potential for a direct current generation were selected. Thus, the selection and classification of these materials that will come to compose the electrolytes were marked by slightly acid pH (5-6) as well as by their electrical conductivity. The three materials that presented a better performance in questions of conductivity and alkaline pH, underwent an analysis of the content of Calcium and Magnesium, which even makes good salts in electrolytes. After the characterization tests, electrochemical cell systems composed of copper and zinc electrodes and the three materials selected as electrolyte were assembled. The results showed that the leaves of lemon, tangerine, and orange present a potential for energy generation. In an open circuit test composed of sixteen electrochemical cells with lemon leaves presented an average potential of 7 V.

KEYWORDS: *Micro power generator, Batteries, Electrolyte, Organic substrate*

I. INTRODUCTION

The patterns of generation and consumption of energy are based on fossil sources, in addition to their finitude, this type of source generates emissions of pollutants among other problems. It is necessary to change the standards by stimulating renewable energy, as well as research on energy innovation. [1]

With the advancement of technologies and society's demand, generators and energy accumulators become more and more present in everyday life.[2] These systems are composed of heavy metals as well as in some cases toxic materials. Thus, it becomes relevant to research alternative materials for the composition of these electrochemical systems.[3] It is observed a tendency of micronization of electrical and electronic products, with low energy consumption, where batteries like the one of the present research, have great application.[4]

That in many places the electric energy is not present, due to problems of distribution, generation or logistics, in these areas microgeneration can contribute to its access. Still, photovoltaic systems wind micro generators, micro turbines and electrochemical systems are the best way to dissipate and meet regions where there is an energy limitation.[5]

Considering that there is an increasing demand for consumer goods, there is a need for a rational use of materials management.[6]. It was created a hierarchy (Figure 1) whose objective is to achieve the maximum practical benefit of the products and to generate the minimum possible amount of waste.[7]

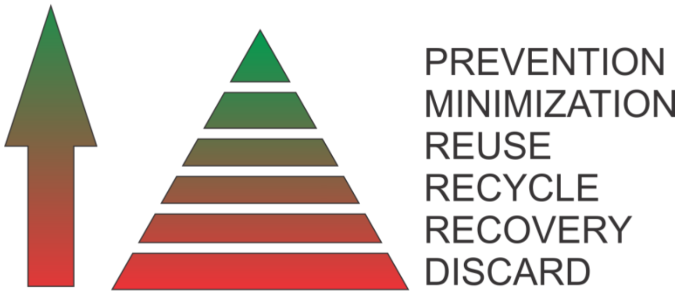

FIGURE 1. Hierarchy of waste management. Adapted [7].

The most important concept of the hierarchy is the prevention of waste generation, for that one of the primary factors is the selection of materials that favor improvements in the processes, as well as the impediment of premature disposal of the products.[7,8] That is when hierarchizing waste management aims to achieve the maximum use of the product, generating the least possible amount of waste.
One of the ways of diversifying forms of energy supply is micro-generation of energy, which is the production of low-carbon, low-carbon electricity.[9,10] There is a demand for the development and use of alternative micro sources, especially for applications that require low consumption.
Microgeneration can serve regions where electricity distribution does not occur. The micro sources bring a socioeconomic balance to the void from the lack of electricity.[11]
But for energy to be part of everyday life, its storage and portability become fundamental. [12].Thus, for an effective way to meet these requirements, accumulators, batteries, based on chemical reactions of toxic metals have been developed. As for example, lead-acid and nickel-cadmium batteries, the most popular systems for providing adequate electrical power to the equipment. [13]
A battery consists of one or more electrochemical cells, connected in series or in parallel, or both, depending on the desired voltage and production capacity. Popular usage considers the " battery " and not the " cells " to be the product that is sold or supplied to the user. [14]
Batteries are being developed to power an increasingly diverse range of applications, from cars to microchips [15]. One problem with the use of batteries is that many have heavy metal contents, and in some cases this type of product leaks easily and heavy metals, as they do not degrade, end up contaminating soil, water, and the entire ecosystem.[16]
Therefore, research in this area is necessary; both for the search for more economical alternatives and for other ways that are not so aggressive to the environment, contributing to the final consumer can choose an environmentally friendly product. [17]
Low-cost voltaic cells can be constructed using commonly available plant materials. In these plant materials, there are several types of organic and inorganic electrolytes.[18] Plant extracts can be used as electrolytes because all plant materials contain various types of inorganic and organic electrolyte substances that are absorbed and used by plants. [19]
In this way the present research had as objective to generate technical-scientific information of the electrical potential obtained from cells of energy formed with electrolytes composed of substrate of natural origin that can potentiate its use in the design of electronic products, contributing to the existing demand of micro energy and portable power generating systems. The present research was organized in the following stages: preparation, physical-chemical characterization and tests of organic materials as electrolytes of an electrochemical system.

EXPERIMENTAL

2.1 MATERIALS AND SAMPLE PREPARATION

Aqueous electrolytes may be alkaline, neutral (slightly acidic) and acidic. "Citrus" is rich in citric acid, ascorbic acid, phenolic compounds, flavonoids, limonoids, and salts, as a criterion for the selection of natural materials. In addition to the citrus selected plants with dark green leaf, this coloring characterizes that in its composition there are salts that possibly will provide good characteristics to compose the electrochemical system. [20,21]
In this way, the leaves of the following materials were selected: Lemon, Orange, Tangerine, Pitanga, Hibiscus, Avocado, Plum, Mulberry, Peach, and Guava. Thus, these sheets tend to fit the basic criteria of a sustainable product, that is, economy, society, and the environment, which are the guiding principles for the Ecodesign applied to the product design.

The selected materials were comminuted (Figure 2) using a Cadence blender (four blades), from the Materials Design and Selection Laboratory (LdSM / DEMAT / EE / UFRGS). In addition to enabling better compression, the comminution increases the contact surface of the material with the other materials that will make up the electrolytic system.

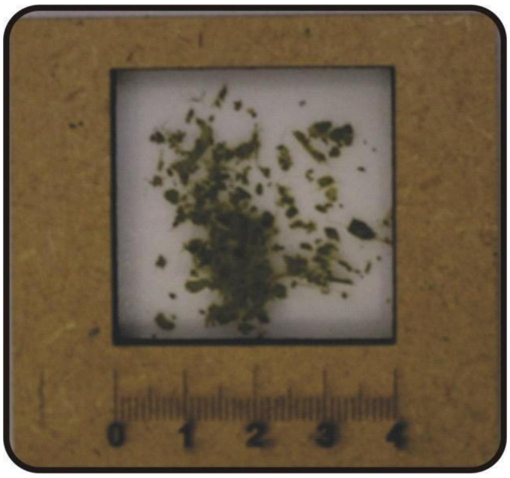

Figure 2. Comminuted Sample

In addition, the crushing facilitates the release of water from the leaves, helping in the structuring of the electrochemical system.

2.2 MATERIALS CHARACTERIZATION

PH MEASUREMENT

For the electrometric determination of pH, 10 g of the sample was weighed in 250 mL beaker, and 100 mL of deionized water was added. The solution was subjected to constant stirring for 30 minutes. After this process the solubilized sample was allowed to stand for 10 minutes, the supernatant was drained to a beaker and pH was measured using a portable pH / ORP / mV potentiometer model 8651 of the brand MARACA AZ, immediately after calibration of the equipment. The pH values were sorted, from more acidic to more alkaline ph to facilitate subsequent selection.

CONDUCTIVITY MEASUREMENT

The conductivity was measured using a W12D conductivity meter from the Bel's brand. For this purpose, 10 g of the sample was weighed into 250 mL beakers and 100 mL of deionized water was added. The solution was subjected to constant stirring for 30 minutes. After this process the solubilized sample was allowed to stand for 10 minutes, the supernatant was drained to a beaker and the measurement was performed. The results, as well as the pH, were ordered.

DETERMINATION OF CALCIUM AND MAGNESIUM IN CRUSHED LEAVES

Preparation of solutions

The EDTA salt was dried at 70 ° C for one hour, after cooling in the desiccator, 3.52 g was transferred to a 1 L flask and solubilized with deionized water.

For the standard Calcium solution, 2.5 g of calcium carbonate (CaCO3), diluted with 100 mL of 4N HCl and weighed into a 1L flask was charged and the volume was quenched with deionized water.

To the standard magnesium solution, 3.5 g of Magnesium Carbonate and solubilized with HCl (4N) were weighed, the solution was transferred to a 1 L flask and the volume filled with deionized water.

Standardization of Ca and Mg

A 5 mL aliquot of the calcium solution was added, to which was added 100 mL of deionized water, 2 mL of NaOH solution (0.2 M), 2 mL of 5% KCN solution, 5 drops of triethanolamine (TEA) and 5 drops of 1% Calcon solution in a 250 mL Erlenmeyer flask. Titrate with the EDTA solution (0.01 M) until the solution becomes blue.

To standardize the Mg, a 5 mL aliquot of magnesium solution was withdrawn, 100 mL of deionized water, 10 mL of pH 10 buffer solution, 2 mL of 5% KCN solution, 5 drops of triethanolamine (TEA) and 6 drops of eriochrome T Black in a 250 mL Erlenmeyer flask. Titrate with the EDTA solution (0.01 M) until the solution becomes blue.

Analysis

The 1g of the ground leaves of each of the materials was transferred to a porcelain crucible and incinerated at 480 ° C until white ash was obtained. The ash was solubilized with 10 mL HCl (1: 1) and placed in a water bath until dry, the dried material re-solubilized with HCl solution (1: 9) and heated to boiling then filtered. The solution was transferred to a 100 mL flask and the volume was quenched with deionized water after cooling.

A 50 mL aliquot was transferred to a 250 mL beaker and 3 mL ferric chloride (with about 1 mg Fe +3.1 mL acetic acid (1: 1), 2 drops methylene red at 0, 1% and a few milliliters of ammonium hydroxide solution (NH4OH) (1: 3) until the solution became yellow and an excess of 1 ml was added. The solution was then heated to boiling and boiled for 5 min. The material was further hot-filtered and the solubilized solute in a 100 mL flask with deionized water.

Again, a 50 ml aliquot was transferred to a 250 ml Erlenmeyer flask, completed the 100 ml volume, 4 ml 20% Sodium Hydroxide, 2 ml 5% KCN solution, 5 drops of triethanolamine and 5 drops of Calcon 1%. It was cast with the 0.01 M EDTA solution until the solution turned blue. The spent volume of EDTA is multiplied by the factor 0.4 by supplying the amount of Calcium in the aliquot.

For determination of magnesium a new aliquot of 50 ml was transferred to a 250 ml Erlenmeyer flask, the volume of 100 ml was added, 5 ml of buffer solution pH 10, 2 M of 5% KCN, 5 drops of triethanolamine (TEA) and 6 drops of 0.5% eriochrome black T. Titrate with 0.01 M EDTA solution until the solution turns blue, the difference in the volume spent in the titration with the volume spent in calcium titration, multiplied by the correction factor of 0.24, provides the amount of magnesium.

II. DESIGN OF THE ELECTROCHEMICAL SYSTEM

Initially, an electrochemical system (1-SE) was constructed, composed of limed leaves, orange, bergamot, plum and hibiscus, copper wires and aluminum wires. The crushed leaves were packed into a cylindrical polymer tube with a lid and 13 cm long and 1.5 cm in diameter, where the experimental pile was assembled. The results obtained demonstrated the potential for power generation as the use of this type of container.

After this, we started to reduce the volume of natural material, because one of the premises of the research is to reduce as much as possible the volume of natural material used. In this sense, Figure 3 presents the arrangement of a system (2-SE) with dimensions of 8 cm in length x 0.7 cm in diameter.

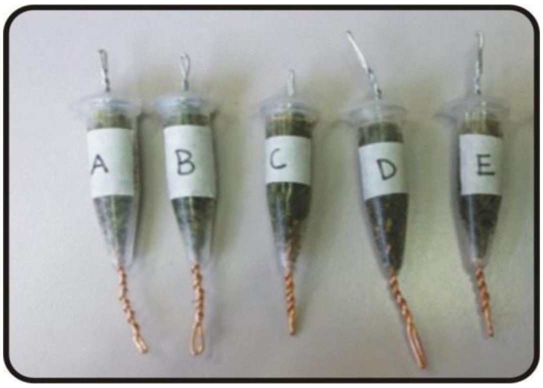

Figure 3. Electrochemical system with lower volume of leaves

Monitoring was carried out for a period of 80 days, where the voltage was measured and the degradation of the material was observed.

When comparing the data obtained between the 1-SE and 2-SE systems, it was observed that the volume reduction did not interfere in the system voltage. In light of these findings, the design of a compact electrochemical system was sought, taking into consideration a cylindrical geometric shape. This form was chosen due to the formal tendency of commercially available batteries, as shown in Figure 4.

For the preliminary tests, a system was built containing 16 cylindrical modules 8 mm in diameter by 6 mm in height, made of acrylic (Figure 4a, 4b), these modules were connected in series to obtain a higher voltage value.

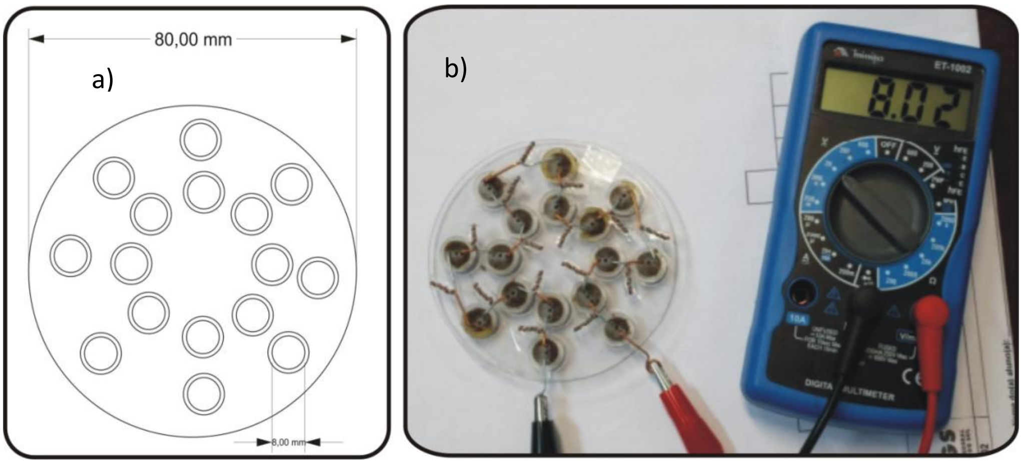

Figure 4. Arrangement of electrochemical cells, (a)Technical design of the arrangement of electrochemical cells, (b) - System in operation.

Figure 4(a) shows the schematic drawing of the system with its dimensions, while Figure 4(b) shows the closed system, its voltage measured with a potentiometer.

III. Results And Discussion

PH MEASUREMENT

Table 1 shows the measured pH values of the ten materials selected for research.

Table 1. pH values

Material	pH
Pitanga	5,65
Mulberry	6,34
Peach	6,40
Plum	6,56
Avocado	6,73
Guava	6,75
Hibiscus	6,99
Orange	7,71
Tangerine	8,15
Lemon	8,38

According to the theoretical references, the developed electrochemical system will use neutral to slightly alkaline electrolytes, to choose, the materials were ranked according to the pH value, the materials chosen are those with pH in the range of 7 to 8, besides the analysis conductivity.

CONDUCTIVITY MEASUREMENT

Table 2 shows the measured conductivity values of the ten materials selected for research, at a temperature of 20 ° C:

Table 2. Conductivity values

Material	μS
Plum	1056
Peach	1156
Avocado	1225
Pitanga	1529
Guava	1533
Hibiscus	1599

Mulberry	1748
Lemon	1895
Tangerine	2140
Orange	2320

It is observed that the electrolytes that have a higher conductivity value are also those in the desired pH range: Lemon, Tangerine, and Orange.

DETERMINATION OF CALCIUM AND MAGNESIUM BY EDTA METHOD

As a supporting analysis, the determination of calcium and magnesium, from materials with neutral to slightly alkaline pH (pH 7-8) was performed, according to the methodology previously explained, Table 3 presents the results:

Table 3. Magnesium and Calcium Concentration in leaves

Material	Ca Content (mg L^{-1})	Mg Content (mg L^{-1})
Lemon	3,32	0,270
Orange	3,31	0,298
Tangerine	3,70	0,325

It is noted that the materials have in their composition similar concentrations of the salts. This analysis ratifies the literature review and indicates the possibility of using these substrates as electrolytes.

ENERGY GENERATION IN THE ELECTROCHEMICAL SYSTEM

For the construction of an energy cell, of the five materials that presented slightly acidic pH, the leaves of lemon, orange, and bergamot, hibiscus and plum were selected. It is noteworthy that the leaves of hibiscus when comminuted have a gelatinous texture, while the plum leaves have low moisture content. According to the presented methodology, the voltage values were tabulated in Table 4.

Table 4. Open circuit potential values over time

Reading	Tangerine (V)	Lemon (V)	Orange (V)
1	0,78	0,80	0,76
2	0,79	0,81	0,77
3	0,79	0,81	0,76
4	0,78	0,80	0,77
5	0,79	0,80	0,74
6	0,77	0,79	0,74
7	0,77	0,79	0,73
8	0,74	0,78	0,70
9	0,73	0,78	0,71
10	0,74	0,77	0,68
11	0,72	0,78	0,69
12	0,69	0,76	0,68

13	0,69	0,76	0,66
14	0,67	0,75	0,65
15	0,68	0,76	0,63
16	0,67	0,73	0,63
17	0,67	0,70	0,62
18	0,66	0,69	0,60
19	0,64	0,68	0,57
20	0,64	0,69	0,54
21	0,63	0,66	0,54
22	0,64	0,66	0,48
23	0,62	0,63	0,44
24	0,59	0,64	0,44
25	0,58	0,63	0,41
26	0,58	0,60	0,42
27	0,58	0,60	0,38

The readings were taken for a period of 78 days. It was observed that the tension generated was relatively low, the lemon and bergamot leaves presented better performance as well as greater stability.

ELECTROLYTE VOLUME REDUCTION

Five electrochemical cells were assembled, each with a material as the basis for the electrolyte and the following values are obtained which are expressed in Table 5.

Table 5. Open circuit potential values over time with a volume of 4 cm^2

Reading	Lemon (V)	Tangerine (V)	Orange (V)
1	0,81	0,79	0,77
2	0,81	0,80	0,79
3	0,80	0,78	0,77
4	0,81	0,78	0,75
5	0,79	0,76	0,75
6	0,78	0,71	0,72
7	0,77	0,68	0,71
8	0,76	0,68	0,67
9	0,74	0,64	0,64
10	0,72	0,60	0,64
11	0,70	0,61	0,60
12	0,68	0,59	0,59
13	0,65	0,59	0,55
14	0,65	0,55	0,55
15	0,62	0,54	0,54

16	0,63	0,53	0,52
17	0,60	0,51	0,49
18	0,59	0,49	0,48
19	0,56	0,45	0,45
20	0,56	0,45	0,42
21	0,54	0,44	0,42
23	0,51	0,41	0,41

The results presented values similar to the first system (1-SE), with a larger leaf volume, having an average standard deviation of 0.102195, indicating a consistency in the measured tension. When comparing the results of the lemon leaves of the first test, where a tube with a larger number of leaves was assembled with the second test, a smaller volume of leaves, it is noticed that in both large and small size similar to those of voltage, however, the batteries with greater quantity of material (the large ones), present a reduction of the tension slower in relation to the smaller ones. Soon the cycle of discharge of the battery in a system with crushed leaves will be directly proportional to the volume of leaves used.

EFFICIENT ARRANGEMENT

For a preliminary essay of an efficient arrangement, the system proposed in the methodology was assembled and as the substrate was used the lemon leaves. The values of the open circuit potential were measured and tabulated as can be seen in Table 6

Table 6. Potential measurements of the electrochemical cell array

Reading	Open circuit potential values (V)
1	7,8
2	8,7
3	8,0
4	9,1
5	8,9
6	8,9
7	8,6
8	8,6
9	8,2
10	7,5
11	7,3
12	7,5
13	7,3
14	7,2

With this arrangement of 16 associated cells, there was a considerable increase in the voltage generated by the system, in addition, the voltage drop as a function of time was attenuated, in the period of about 50 days the measured maximum voltage was 9.1 V and the minimum of 7.2 V, generating an average of 8.11 V with Standard Deviation of 0.682594.

IV. CONCLUSION

Ten organic materials were selected for testing as electrolytes. Of the ten materials, the leaves of lemon, tangerine, and orange had the best conductivity values: 18895µS, 2140µS and 2320µS respectively. These three materials also had desirable pH values in the range 7-8. When checking for calcium, the lemon, tangerine, and orange leaves had a content of 3.32

mg. L^{-1}, 3,31 mg. L^{-1} and 3.70 mg. L^{-1} , respectively, already the values of magnesium content, were around 0.3 mg. L^{-1}. Indicating potential to be used as electrodes.

When tested as electrolytes the three materials, lemon, tangerine, and orange leaves presented similar performances, and the lemon obtained a better performance with an open circuit potential value in the range of 0.7 V, in addition, with the in the course of time, the electrolyte with lemon leaves showed greater stability.

The use of the association of 16 electrochemical cells with lemon leaves as an electrolyte, in series, obtained considerable results, besides a stability in the 7V range of open circuit potential.

According to the analyzes, the potential of the use of organic materials as electrolytes for microgeneration of energy was verified, it is highlighted that the lemon leaves were the ones that presented the best results, providing conditions to act as electrolytes in an electrochemical system.

V. FUTURE WORK

For future work, perform the ohmic analysis. Other analysis in a closed circuit. Test mixtures of these substrates in the electrolyte composition.

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