# BATTERY DESIGN: NATURAL MATERIALS FOR ENERGY MICROGENERATION

Dalarosa, Regiane[1] Fernandes, Carolina Fernandes[2] and
Cândido, Luis Henrique Alves[3]
[1]Graduate Program in Design, Laboratory of Design and Material Selection, Federal University of Rio Grande do Sul, UFRGS, Av. Osvaldo Aranha, n.99, 604, Centro Histórico, Porto Alegre, Brazil.
*regiane.dalarosa@ufrgs.br*
[2]Graduate Chemical Engineering, Laboratory of Design and Material Selection, Federal University of Rio Grande do Sul, UFRGS, Av. Osvaldo Aranha, n.99, 604, Centro Histórico, Porto Alegre, Brazil.
*fernandes.fernandes@ufrgs.br*
[3]Departament of Design and Graphic Expression, Laboratory of Design and Material Selection, Federal University of Rio Grande do Sul, UFRGS, Av. Osvaldo Aranha, n.99, 604, Centro Histórico, Porto Alegre, Brazil.
*candido@ufrgs.br*

## *ABSTRACT*

*Technological advances in portable electronic devices and their consumption pattern has stimulated the demand for smaller-sized, more efficient batteries. However, the tradeoff of the materials components of the batteries are heavy metals and present high toxicity, which brings about safety of use and disposal concerns. One of the components of the batteries involving important environmental and safety impacts are the electrolytes; for example, sulfuric acid, highly reactive and corrosive to metals and skin, present in lead-acid batteries widely employed in automobile industry. As an alternative electrolyte, this work presents the physical-chemical and electrochemical characterization of just-extracted orange juice as battery electrolyte, considering its renewable source, high availability and easiness of disposal. Juice has been studied from three fruit Citrus sinensis species: "Valência", "Navelina" and "Céu". The best performance corresponded to "Valência", whose pH was the lowest (3.37) and conductivity the highest (4.16 mS); in addition, this electrolyte developed the highest potential difference between Cu and Zn (0.9 V).*

***KEYWORDS:*** *Energy microgeneration, Eco design, Battery, Battery electrolyte, Orange juice.*

## I. INTRODUCTION

Technology has eased the people routine with the employment of useful devices that help during quotidian activities, like portable electronics [1], wearable technology [2] and microchips [3]. Thus, the mobility of those devices requires smaller and more efficient conversion and store energy components [4]. The International Data Corporation (IDC) foresees that 240 million portable devices, like smart clothes and watches, will be available to consumers in 2021[2, 5]. Aiming to satisfy the growing energy demand of these devices, the use of batteries has increased, with the worry of their safe use and disposal due to the heavy metals and dangerous electrolytes that are part of them [15], as in the lead-acid and nickel-cadmium batteries [6].

In consequence, diverse organizations and researchers from different expertise have discussed the use of new materials as alternative renewable energy sources as substitution for fossil fuels [7], aiming sustainability [8]. In 2015, United Nations established an agenda with goals for sustainable development to fulfill until 2030; one of the goals pursuits to "ensure access to affordable, reliable, sustainable and modern energy for all" [9]. Through this goal, UN remarks the need for alternative energy sources and recognizes that about 1.3 billion people has not access to electricity [9].

Solar and wind energy have been widely studied as renewable sources alternative to fossil fuels, due to their abundance and availability [10]. However, they involve important costs of distribution especially for farthest, almost isolated regions; for this application, energy microgeneration presents an interesting alternative. Energy microgeneration consists in the low-carbon electricity production, for which obtaining materials easily found in nature can be employed, which means the possibility of electricity access in hard-to-reach places [6]. With the investment in diversity of energy sources, sustainable production growth and the increase of the electricity offer can be expected [11]. In this way, consumers can choose among more environmentally friendly options and sustainable technologies will be more accessible to people in general [6-10].

Recently, new materials have been explored as low-toxicity battery electrolytes [7]. The electrolyte is responsible for the electrical energy conversion and storage and is commonly based on hard-to-manipulate and hard-disposal substances [22]. Simulated human sweat have been studied as electrolyte for wearable flexible batteries among those alternative electrolytes [2]. Jell-O based micro batteries, with non-corrosive electrolyte, have also been considered as highly safe, low-cost alternatives for ingestible micro devices in medicine [3]. Other studies have focused on seawater as battery electrolyte for military and commercial purposes [10, 12]. Other natural substrates, such as lemon, tangerine and orange leaves, have also been studied as electrolytes for the design of portable micro batteries [6].

From the design perspective, relationship between the development of electronics and the concept of sustainable development is still under construction, in special the acknowledgment of design environmental impact along the whole product conception until its disposal [13, 14]. In addition, design conceptions do not use to consider environmental variables, which leads to unsustainable scenarios [16]. On the opposite, eco design is based on environmental requirements during product conception and development, like the avoidance of toxic and perilous materials in products and the use of renewable and biodegradable materials.

Following these lines, the aim of this work is to characterize natural orange (*Citrus sinensis*) juice as battery electrolyte for copper – zinc cells. This electrolyte was chosen due to its renewable origin and its availability in Brazil. In 2014, the world production of oranges was of 51 million tonne [19]; 17.8 million tonne were produced by Brazil, which makes of the country the first producer of this fruit [18], followed by the United States [19]. The fruits selected in this study were among the main species of grown oranges in the State of Rio Grande do Sul: “Valência”, “Navelina” and “Céu” (Figure 1) [24]. The “Valencia” variety is intended for fruit consumption and high juice production, due to its acidity. The “Navelina” variety is mainly consumed as fruit, because its juice gets bitter very fast. The "Céu" variety is also mainly consumed as fruit because it is the least acidic variety [24].

Oranges are rich in citric and ascorbic acids, which enhances their electrochemical behavior [20]. Orange juice is also considered non-toxic, renewable and biodegradable. The former properties together with the high availability of the feedstock are key requirements for low environmental impact materials for design [17].

**Figure 1.** Fruit varieties selected for study. a) “Valência” orange b) “Navelina” orange c) “Céu” orange.

This research was organized in the following stages: material selection and preparation, physicochemical characterization of orange juice and electrochemical characterization tests using orange juice as electrolyte in cells with copper and zinc electrodes.

# II. EXPERIMENTAL

## 2.1. Materials selection and preparation

In this study, only natural juice was used. Fruits were acquired from the same supplier. New juice was extracted before each test. Juice preparation was handmade: fruits were washed with water from the municipal distribution supply, cut in two moieties and the juice was extracted aided with a manual extractor. In order to reduce the solid matter and to obtain a more homogeneous juice, 65 mesh filter was employed. An average of 123 ml juice per fruit was extracted; the mean mass of each fruit was of 148 g. After filtration, there was a 14% reduction in juice volume.

## 2.2. Physical-chemical characterization

Physical-chemical characterization of the studied orange juice involved pH and conductivity determination. pH is a measure of acidity of aqueous solutions, being more acidic when values are less than 7.00 and more alkaline when values are higher than 7.00 [6]. pH was measured with Sanxin MP 521 Lab pH/Conductivity Meter at 23 °C; orange juice was stirred before the measurements. Conductivity was evaluated to compare the electrical character of the electrolytes, employing a Bel Engineering W12D Conductivity Meter at 23 °C.

## 2.3 Electrochemical characterization

Two-electrode electrochemical cells were mounted employing Zn and Cu plates with dimensions of 33mmx3mmx1mm as electrodes (purity 99%). Electrodes were chosen given their standard reduction potential values and the availability of the materials. Cells were mounted employing Eppendorf® micro tubes of 1.5 ml; cuts were done on the cover of the micro tube to insert the electrodes. Electrodes were sanded with sanding paper and fixed. A polypropylene separator was used inside the micro tube, given its chemical inertness regarding orange juice, easiness to find and reuse possibility. Open circuit potential (OCP) was monitored with digital multimeter Minipa ET-1002, considering fruit variety, volume of the electrolyte and materials degradation.

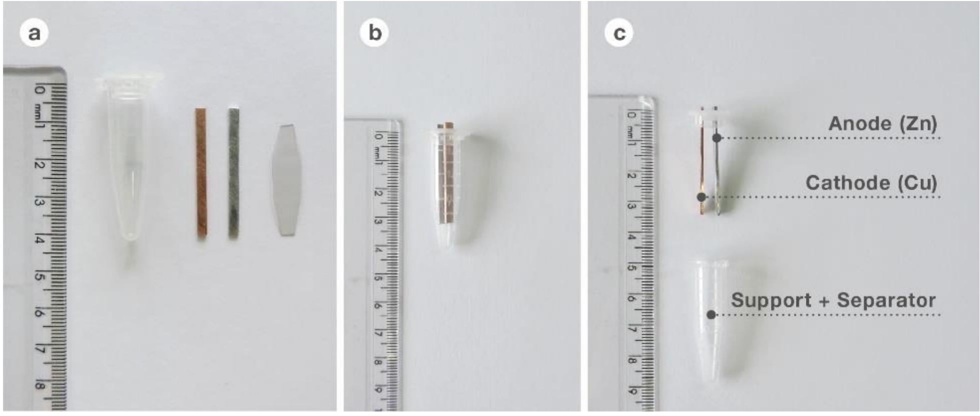

**Figure 2.** Electrochemical cell assembly. a) Cell components b) Mounted cell c) Scheme of the electrodes and separator fixation.

In order to verify the effect fruit variety, an acrylic grid was employed to organize 27 cells as displayed in Figure 3. Each column of the grid corresponds to a different fruit variety; three samples of each variety were placed. 1.5 ml electrolyte was placed in the Eppendorf® micro tube, as shown in Figure 3. For this, the potential was performed a single potential reading.

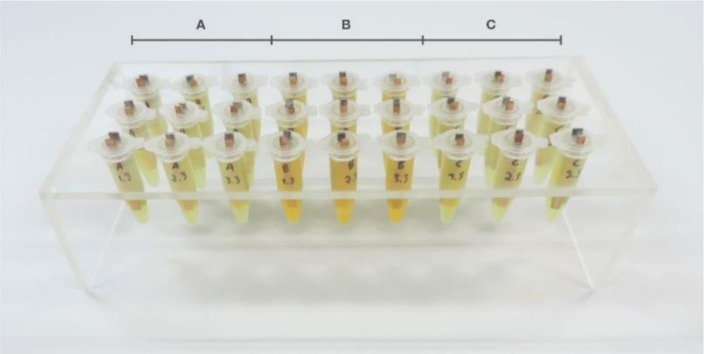

**Figure 3.** Grid for the open circuit potential monitoring of the 27 cells assembled. A: Cells with “Valência” orange juice. B: Cells with “Navelina” orange juice. C: Cells with “Céu” orange juice.

Electrolyte volume influence was evaluated in a 25 cell-grid (Figure 4); 1.5 ml Eppendorf® micro tubes were cut in different dimensions to reach the volumes 1.0 ml, 0.8 ml, 0.6 ml, 0.4 ml and 0.2 ml, with a cutting machine (Buehler IsoMet Low Speed). Five samples were placed to measure the error. Only the juice with the best result (higher OCP) in the experiment of the orange variety influence. OCP was monitored for 15 days, at 23 °C. Despite the electrode area does not affect the OCP [21,22], considering the low-scale energy generation, the goal of this test is to identify the minimum electrolyte amount necessary for the electrochemical reaction to take place.

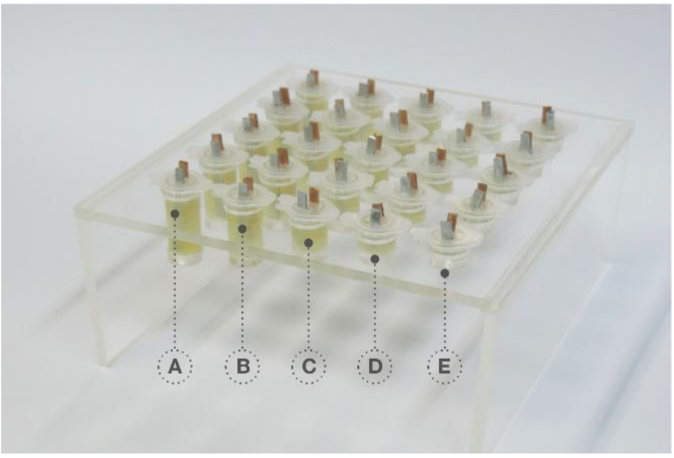

**Figure 4.** Grid for the open circuit potential monitoring of the electrolyte volume variation study:
a) 1,0ml b) 0,8ml c) 0,6ml d) 0,4ml and e) 0,2ml.

Knowing the origin of the electrolyte, during electrochemical reactions, it can suffer any type of degradation. So, aiming to identify possible OCP variation promoted by the electrolyte degradation and electrodes redox processes, 5 cells were prepared (Figure 5) and their OCP monitored for 15 days. 1.5 ml juice in Eppendorf® micro tubes were employed. Mass of the electrodes was measured with analytical balance (Quimis Q500l210c) before and after the immersion test. Only the juice with the highest OCP was tested. Samples were maintained at temperature of 23 °C.

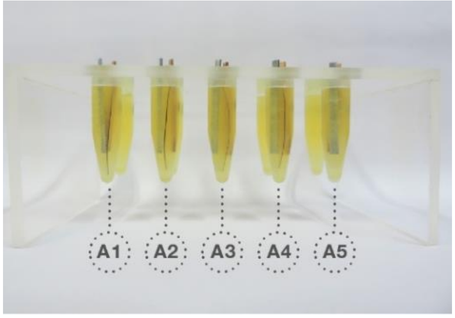

**Figure 5.** Grid for monitoring open circuit potential of material degradation study.

# III. RESULTS AND DISCUSSION

## 3.1 Physical-chemical characterization

pH and conductivity of the electrolytes are presented in Table 1. For the fruits of “Valência” and “Navelina” varieties pH values were acidic; meanwhile, Céu varity pH was neutral. All juices had important conductivity values; however, juice extracted from “Valência” oranges presented the highest conductivity, “Navelina” the intermediate value and “Céu” was the less conductive electrolyte. Due to these properties, the electrolyte with better perspective to be a good electrolyte is the “Valência” juice, since its lower pH is highly desirable for battery applications because acidic electrolytes promote anode oxidation, as well as its high conductivity, which allows ionic transport [6].

**Table 1.** pH and conductivity for the juices of the three studied varieties.

| Sample | pH | Conductivity (mS) | Temperature (°C) |
|---|---|---|---|
| Valência (A) | 3,37 | 4,16 | 24°C |
| Navelina (B) | 3,60 | 3,20 | 24°C |
| Céu (C) | 6,58 | 2,87 | 24°C |

## 3.2 Electrochemichal characterization

Electrochemical characterization was conducted evaluating the OCP variation influenced by the fruit variety, electrolyte volume and materials degradation. Regarding fruit variety (Table 2), OCP presented good repeatability for the replicates when employing the same orange variety, which can be related to uniformity of composition of the orange units of each variety. Cell potential when in presence of “Valência” oranges was the highest: 0.91 ± V. Meanwhile, “Navelina” and “Céu” varieties presented average OCP of 0.87 V and 0.81 V in this order, having an average standard deviation of 0,047134. These values are in agreement with those of pH and conductivity. In consequence, the following tests will be conducted with juice coming from “Valência” orange.

**Table 2.** Open circuit potential of the three fruit varieties.

| Valência (A) | | | Navelina (B) | | | Céu (C) | | |
|---|---|---|---|---|---|---|---|---|
| **A1** | **A2** | **A3** | **B1** | **B2** | **B3** | **C1** | **C2** | **C3** |
| 0.93 | 0.90 | 0.94 | 0.82 | 0.89 | 0.86 | 0.82 | 0.82 | 0.81 |
| 0.91 | 0.90 | 0.94 | 0.87 | 0.89 | 0.88 | 0.82 | 0.82 | 0.81 |
| 0.90 | 0.91 | 0.92 | 0.89 | 0.87 | 0.89 | 0.80 | 0.80 | 0.80 |

When the electrolyte volume influence was evaluated (Figure 6), cell potential (V) during the first measurement the OCP values were the same, close to 0.9 V. But after 8 days, the sample with the lowest volume (0.2 ml) presented 0.0 V. Cells with 0.4 ml and 0.6 ml developed important OCP oscillations after 8 days; meanwhile cells with 1.0 and 0.8 ml were very stable along the whole experiment and closer to the initial 0.9 V. Despite the electrolyte volume does not affect initially the OCP value of the cell [22], with time, OCP tends to lose its stability, which means, the reduction of the useful life of the battery. It takes place due to the consumption of the species involved in the redox reaction as well as the increase of the ohmic drop.

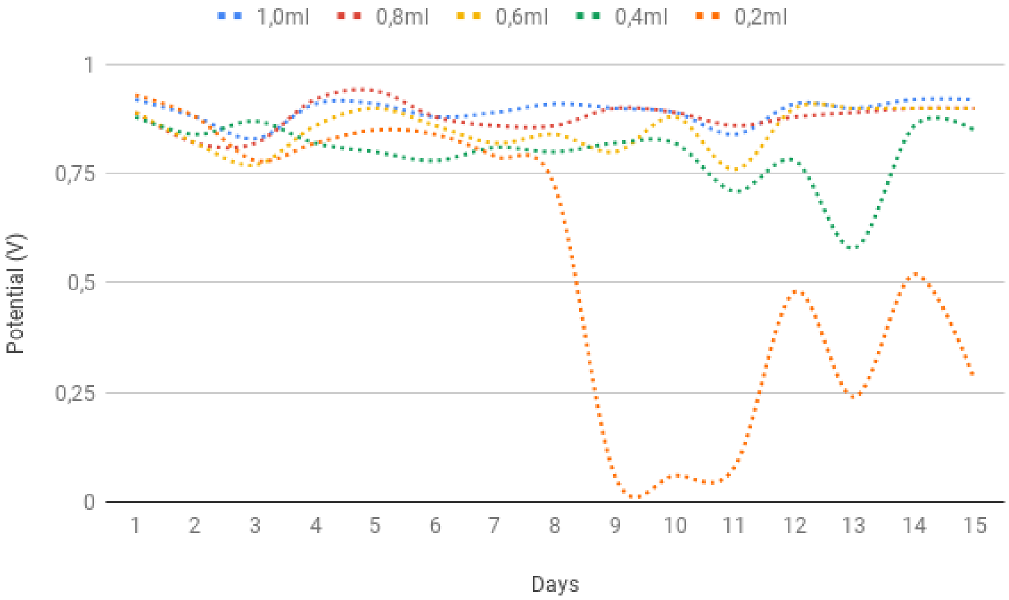

**Figure 6.** OCP for cells with different electrolyte volume.

As observed in the former tests, the cells with more volume of electrolyte developed better, stable performance when compared to the other ones. Therefore, this was the established volume for cell sizing. In order to evaluate the influence of the electrodes and electrolyte materials degradation, OCP was monitored for 15 days. All cells displayed the same OCP pattern: cell potential was stable until 10th day; after this time, cell potential oscillated between 0.9 V and 0.0 V, due to the modification of the juice components and the redox processes that take place in the electrodes.

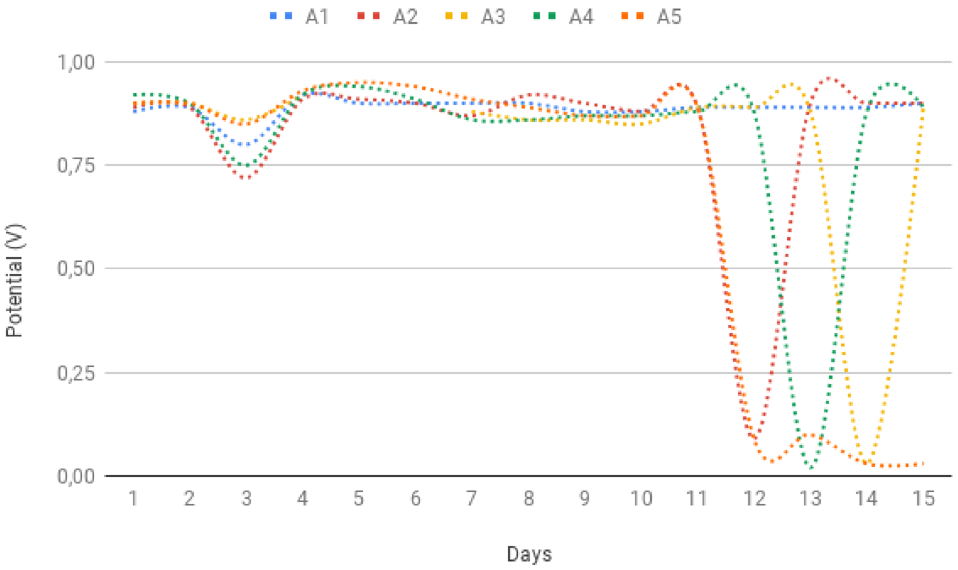

**Figure 7.** Evaluation of the influence of the electrode degradation on cell OCP.

Aiming to estimate the presence of redox processes, mass loss was determined, and the results appear in Table 3. An average reduction of 2.62% for the Zn electrodes and 0.41% for the Cu plates were found. The important mass loss at the Zn electrode is explained by the dissolution of this metal towards the electrolyte; on the other hand, Cu suffers reduction, which consists in electron accepting by the cathode. This mass variation confirms the processes of corrosion of Zn (chemical energy) to produce electrical energy. Sample A5 presented the lowest mass loss, maybe because it reached 0.0 V before the other samples could. Samples A1 – A4 developed 1.5 V even at the end of the experiment.

**Table 3.** Mass (g) of the electrodes before and after immersion for 15 days in orange juice.

| Sample | Initial mass (g) | | Final mass (g) | | Mass loss (%) | |
|---|---|---|---|---|---|---|
| | Zn | Cu | Zn | Cu | Zn | Cu |
| **A1** | 0.5024 | 0.7801 | 0.4904 | 0.7766 | 2.38% | 0.44% |
| **A2** | 0.4958 | 0.7083 | 0.4826 | 0.7059 | 2.66% | 0.33% |
| **A3** | 0.5078 | 0.7975 | 0.4854 | 0.7946 | 4.41% | 0.36% |
| **A4** | 0.5070 | 0.7879 | 0.4963 | 0.7820 | 2.11% | 0.74% |
| **A5** | 0.4994 | 0.7377 | 0.4917 | 0.7361 | 1.54% | 0.21% |

## IV. CONCLUSIONS

Orange juice coming from three different orange varieties has been tested as electrolyte for Cu-Zn battery. The best performance among the studied varieties corresponded to “Valência” orange, whose pH and conductivity were the highest when compared to the juices of “Navelina” and “Céu” varieties. “Valência” orange juice promoted the highest potential difference for the Cu-Zn couple, 0.9 V. The cell employing this juice kept this potential for 10 days with 1.5 ml electrolyte. In addition, 0.2 ml was enough volume to produce energy in low scale for 8 days. These results allow proposing new low-cost alternatives to diversify the energy sources and to turn it more accessible. For this reason, design professionals and researchers play an important role at the materials selected for the energy generation devices, to supply more environmentally friendly and more accessible technologies for battery design.

## V. FUTURE WORKS

Future works point out the cell association for obtaining high voltages or current, useful life determination of the battery and the possibility of juice refill, the evaluation of wasted orange juice because it is considered improper for consumption, and the development of a portable device that can be easily fed with natural electrolytes available in nature.

## ACKNOWLEDGEMENTS

Authors acknowledge technicians and professors of the Material Design and Selection Laboratory (LDSM) and Corrosion Research Lab (LAPEC) at Federal University of Rio Grande do Sul (UFRGS) that contributed to conduct this study. Authors also thank Higher Education Personnel Improvement Coordination (CAPES), Brazilian agency for Higher Education financing, for the financial support.

## REFERENCES

[1].KIM, Y.; KIM, H.; PARKA, S.; SEOB, I. Na ion-Conducting Ceramic as Solid Electrolyte for Rechargeable Seawater Batteries. Electrochimica Acta, DOI:10.1016/j.electacta.2016.01.054, v. 191, pp. 1-7, 2016a.

[2].VILKHU, R; THIO, W. J. C.; GHATAK, P.; SEN, C. K.; ANNE, C.; KIOURTI, A. Power Generation for Wearable Electronics: Designing Electrochemical Storage on Fabrics. Special Section on Wearable and Implantable Devices and Systems. 2018. DOI: 10.1109. ACESS 2018.2839078.

[3].CRESPILHO, F. N.; SEDENHO, G. C.; PORCELLINIS, D.; KERR, E.; FOCIL, S. G.; GORDON, R.G; AZIZ, M. J . Non-corrosive, low-toxicity gel-based microbattery from organic and organometallic molecules. Journal of Materials Chemistry A, [s.l.], v. 7, n. 43, p.24784-24787, 2019. Royal Society of Chemistry (RSC). DOI: 10.1039/c9ta08685d.

[4].MICHELINI, A. Baterias Recarregáveis para equipamentos portáteis. 1º Ed. STA: São Paulo, 2017.

[5].International Data Corporation. Worldwide Wearables Market to Nearly Double by 2021, According to IDC. Accessed: Jul, 2019. [Online]. Available: < https://bit.ly/2OZBe2n>.

[6].FINAMOR, J. N. S.; CÂNDIDO, L. H. A. Microgeneration of energy with electrolyte use organic substrato compounds. International journal of advances in engineering & technology. v.10, n. 5, p. 541-550. Oct, 2017.

[7].ANGELL, M; CHUN, J. P.;YOUMIN R.; CHUNZE, Y.; MENG, C. L.; BING, J. H; HONGJIE, D. High Coulombic efficiency aluminum-ion battery using an AlCl3-urea ionic liquid analog electrolyte. Proceedings of the National Academy of Sciences, [s.l.], v. 114, n. 5, p.834-839, 17 Jan, 2017.

[8].WORLD COMMISSION ON ENVIRONMENT AND DEVELOPMENT. Our Common Future. Oxford University Press, 1987.

[9].ORGANIZAÇÃO DAS NAÇÕES UNIDAS. ONU. Os novos 17 Objetivos de Desenvolvimento Sustentável da ONU. 2015. Accessed: Jul, 2019. [Online]. Available: <https://bit.ly/1Qux9gU>.

[10]. SUSANTO, A.; MULYONO, S. B.; SUGENG, H. W.; MOCHAMMED, R.; FIS, P. Seawater battery whit Al-Cu, Zn-Cu, Gal-Cu Electrodes for Fishing Lamp. International Journal of Renewable Energy Research. Indonesia, v. 7, n. 4, 2017.

[11]. SITHAN, M.; LAI, L. L. Application of green technologies in developing countries-reduced carbon emission and conservation of energy. In: 2011 IEEE Power and Energy Society General Meeting. IEEE, 2011.

[12]. ZHAO, H; BIAN, P.; JU, D. Electrochemical performance of magnesium alloy and its application on the sea water battery. Journal of Environmental Sciences. ISSN 1001-0742. 2009.

[13]. PLATCHECK, E. R. Design industrial: metodologia de EcoDesign para o desenvolvimento de produtos sustentáveis. São Paulo: Atlas, 2012.

[14]. PLATCHECK, E. R.; SHAEFFER, L.; KINDLEIN JUNIOR, W.; CÂNDIDO, L. H. A. Methodology of ecodesign for the development of more sustainable electro-electronic equipments. Journal of Cleaner Production, v. 16, Issue 1. Jan, 2008.

[15]. REIDLER, N. M. V. L.; GÜNTHER, W. M. R. Impactos ambientais e sanitários causados por descarte inadequado de pilhas e baterias usadas. Revista Limpeza Pública, São Paulo, v. 60, 2003.

[16]. JACQUES, J. J. Estudo de iniciativas em desenvolvimento sustentável de produtos em empresas calçadistas a partir do conceito berço ao berço. Thesis (Doctorate in Production Engineering). Postgraduate Program in Production Engineering, Federal University of Rio Grande do Sul, Porto Alegre, 2011.

[17]. MANZINI, E.; VEZZOLI, C. O desenvolvimento de produtos sustentáveis: os requisitos ambientais dos produtos industriais. 4 ed. São Paulo: Edusp, 2016.

[18]. INSTITUTO BRASILEIRO DE GEOGRAFIA E ESTATÍSTICA. IBGE. Produção Agrícola Municipal (PAM). Rio de Janeiro, v. 44, p.1-8, 2017. Accessed: Jun, 2019. [Online]. Available: <https://bit.ly/2MTCWog>.

[19]. USDA - U.S. DEPARTMENT OF AGRICULTURE. Citrus: World Markets and Trade, United States Department of Agriculture, Foreign Agricultural Service. Accessed: Abr. 2019 [Online]. Available: <https://bit.ly/2KSPCHT>.

[20]. LADANIYA, M. S. Citrus Fruit: Biology, Technology and Evaluation. Elsevier, 2008.

[21]. FARIA JUNIOR, R. N.; ZARPELON, L. M. C.; SERNA, M. M. Baterias Recarregáveis: Introdução aos Materiais e Cálculos. ArtLiber 1º Ed. São Paulo, 2014.

[22]. REDDY, T. B. Linden's handbook of batteries. New York: McGraw-hill, 2011.

[23]. CYPRIANO, D. Z.; DA SILVA, L. L.; MARIÑO, M. A; TASIC, L. A Biomassa da Laranja e seus Subprodutos. Virtual Chemical Magazine. v. 9, n. 1, 2017.

[24]. EFROM, C. F. S.; SOUZA, P. V. D. Citricultura do Rio Grande do Sul: indicações técnicas. 1. ed. Porto Alegre: Secretariat of Agriculture, Livestock and Irrigation - SEAPI; DDPA, 2018. Accessed: Jul, 2019. [Online]. Available: <https://bit.ly/2OJUowp>.

## AUTHORS

**Dalarosa, Regiane**. Holds degree in Fashion Design (UNOCHAPECO). Specialist in fashion, creation and communication (UNIVALI). Master student in the Graduate Program in Design and Capes Scholarship at the Design and Materials Selection Laboratory of the Federal University of Rio Grande do Sul (PGDesign/LDSM/UFRGS). Under the guidance of Prof. Dr. Luis Henrique Alves Cândido.

**Fernandes, Carolina Fernandes**. Undergraduate in Chemical Engineering and Capes Scholarship at the Design and Materials Selection Laboratory of the Federal University of Rio Grande do Sul (LDSM/UFRGS). Under the guidance of Prof. Dr. Luis Henrique Alves Cândido.

**Cândido, Luis Henrique Alves**. Holds degree in Industrial Design (Product Design), Masters and Doctorate in Material Science and Technology from the PPGE3M/UFRGS Program. Associate professor of product design (DEG/FA/UFRGS) and teacher of the graduate program in Design (PGDesign/UFRGS).