

Blue Energy Harvesting of Ocean Waves: Optimizing Triboelectric Nanogenerators to Sea States in Integrated Experimental and Multiphysics Modelling

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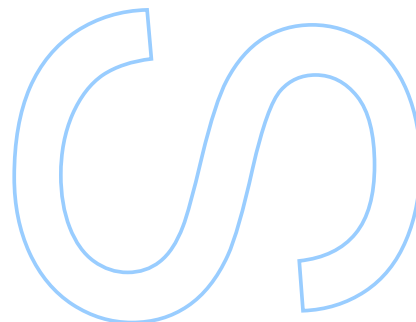
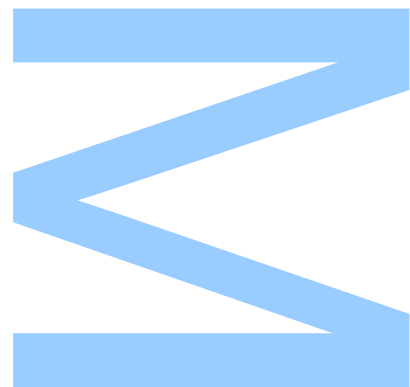
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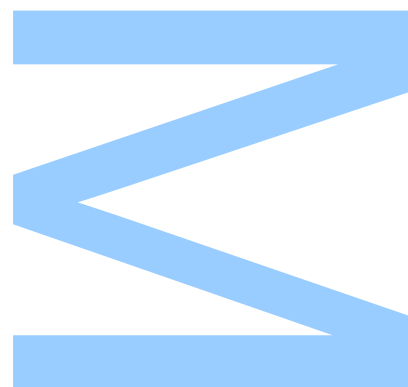




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MASTERS THESIS

**Blue Energy Harvesting of Ocean Waves:
Optimizing Triboelectric Nanogenerators to
Sea States in Integrated Experimental and
Multiphysics Modelling**

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“Beyond work and love, I would add two other ingredients that give meaning to life. First, to fulfill whatever talents we are born with. (...) Second, we should try to leave the world a better place than when we entered it. As individuals, we can make a difference, whether it is to probe the secrets of Nature, to clean up the environment and work for peace and social justice, or to nurture the inquisitive, vibrant spirit of the young by being a mentor and a guide.”

Michio Kaku, in *Parallel Worlds: A Journey Through Creation, Higher Dimensions, and the
Future of the Cosmos*

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Abstract

Faculdade de Ciências da Universidade do Porto

Departamento de Física e Astronomia

MSc. Engineering Physics

Blue Energy Harvesting of Ocean Waves: Optimizing Triboelectric Nanogenerators to Sea States in Integrated Experimental and Multiphysics Modelling

by [Isabel GONÇALVES](#)

Triboelectric nanogenerators (TENGs) are mechanical energy harvesters that use the triboelectric effect present in our everyday life to generate an electrical current through electrostatic induction. From the different sources they are able to harvest, one in particular seems a perfect fit for this technology, due to its sensitivity to low frequency motion, being light weight, low cost and of easy encapsulation: ocean waves. In fact, TENGs tackle with distinction the limitations of traditional electromagnetic wave energy converters, therefore they are considered the future of ocean wave energy harvesting.

As many prototypes are already under development, the optimization of TENGs is of crucial importance, both at the materials and design level, for applications either in distant or very near future. At the materials level, thin films of Poly(tetrafluoroethylene) (PTFE) were fabricated and incorporated on TENGs. Devices with power output $\sim \mu\text{W}$ were obtained for an optimized substrate and thickness, although many questions remained unanswered, paving the way for a more detailed investigation.

Futhermore, a specific TENG based on rolling spheres, fabricated with commercial PTFE, was studied in depth, as it showed an interesting yet unexplained behavior: its power output was larger towards specific motion parameters, predicted to be associated with the impact velocity of the sphere. A multiparametric evaluation of power output was performed along with multiphysics modelling and simulation of the device, that stated a clear relation between the sphere velocity and the increase in power output, confirming our hypothesis. Moreover, from this detailed understanding of the generator behavior, modifications on the design were introduced and a 2-fold increase in power density was

obtained, from 1.9 Wm^{-3} to 4.1 Wm^{-3} . From the confrontation of experimental results on power and the simulations, this work created an advanced tool to design optimized TENGs for particular sea states.

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Resumo

Faculdade de Ciências da Universidade do Porto

Departamento de Física e Astronomia

Mestrado Integrado em Engenharia Física

**Colheita de Energia Azul das Ondas do Oceano: Optimizando Nanogeradores
Trioelétricos a Estados Marítimos numa Modelização Multifísica e Experimental
Integrada**

por Isabel GONÇALVES

Nanogeradores trioelétricos (TENGs) são coletores de energia mecânica que usam o efeito trioelétrico presente no dia-a-dia para gerar uma corrente elétrica por meio de indução eletrostática. Das diferentes fontes que conseguem colher, uma em particular parece adequar-se perfeitamente a esta tecnologia, devido à sensibilidade aos movimentos de baixa frequência, leveza, baixo custo e fácil encapsulamento desta: as ondas do mar. Na verdade, os TENGs ultrapassam com distinção as limitações dos conversores eletromagnéticos de energia das ondas tradicionais, portanto, eles são considerados o futuro da colheita de energia das ondas do mar.

Como muitos protótipos estão já em desenvolvimento, a otimização dos TENGs tem uma importância crucial, tanto a nível de materiais como de design, para aplicações quer num futuro distante quer muito próximo. Ao nível de materiais, filmes finos de Poli(tetrafluoroetileno) (PTFE) foram fabricados e incorporados em TENGs. Dispositivos com potência $\sim \mu\text{W}$ foram obtidos para um substrato e espessura otimizados, no entanto, muitas questões permaneceram sem resposta, abrindo caminho para uma investigação mais detalhada.

Além disso, um TENG específico baseado em esferas rolantes, fabricado com PTFE comercial, foi estudado em detalhe, pois apresentou um interessante, mas inexplicável, comportamento: a potência gerada foi maior para parâmetros de movimento específicos, suspeitando-se de estarem associados à velocidade de impacto da esfera. Uma avaliação multiparamétrica da potência foi realizada juntamente com a modelização multifísica e

simulação do dispositivo, que estabeleceu uma relação clara entre a velocidade da esfera e o aumento da potência, confirmando a nossa hipótese. Além disso, a partir do conhecimento detalhado do comportamento do gerador, modificações a nível de design foram introduzidas, obtendo-se um aumento de 2 vezes na densidade de potência, de 1.9 Wm^{-3} para 4.1 Wm^{-3} . Confrontando os resultados experimentais de potência com simulações, este trabalho criou uma ferramenta avançada para projetar TENGs otimizados para certos estados do mar.

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Chapter 1

Introduction

As the global energy demand increases and the destructive impact of human activities on nature becomes clear, efforts must be done to increase the share of non expensive (hence more accessible), renewable energy - blue energy - in the world energy mix. Moreover, the expansion of technology to our daily lives has driven the development of a multitude of sensors, actuators, wireless communication modules, portable electronic devices, and many other low power gadgets. Operating autonomously and continuously they illustrate the real need, beyond the opportunity, for blue energy harvesting devices.

Note that we are debating energy *harvesting* devices, not energy “*production*” devices. As a wise man once said, in Nature nothing is lost, but transformed - and no energy is created, just transferred. Energy harvesting devices are indeed electrical energy generators, however they do so not by disrupting, drilling or polluting any landscape for the sake of energy (and money), but simply take advantage of everyday available, unnoticed energy sources, at the site of consumption. The harvest is always a time of great joy, when the farmer obtains the results of all his/her dedication throughout the year, after nurturing the crops that, in the end of the day, are our own energy source. In a similar way, the Earth has been nurturing, preserving itself for billions of years, offering us a multitude of renewable sources: the sun, wind and water flow, heat and also human activities as we are an important part of the system, that are just waiting to be collected.

Triboelectric nanogenerators (TENGs) are emerging mechanical energy harvesting devices, in development for only the last 10 years [1–3]. They take advantage of the universally present contact electrification (the culprit of static hair) and operate on the basis of electrostatic induction. They are low cost devices, due to the immense quantity and diversity of materials that can be contact electrified, and they have a cheap fabrication as

well, because their operating principle is very simple. TENGs can harvest any type of vibration (random, periodic, regular, irregular, low frequency or high frequency) with high efficiency [4], having reached a power density of 500 W/m^2 [5] (for comparison, in July 2021 the maximum power density of photovoltaic energy was 247 W/m^2 [6]), and they do not depend on intermittent sources such as other renewable energy harvesters. Potential applications include self-powered devices, environmental monitoring, active sensing [7], wearable electronics and high voltage power sources [8], but there are also ongoing efforts for upscaling the technology [9], which shows its versatility.

On the other hand, the oceans have a great need for robust small energy generators for weather monitoring and forecasting, navigation, oceanography, surveillance, currently not met at all by the most known mechanical energy generator, the electromagnetic converter [4]. As opposed to the electromagnetic converter, TENGs can harvest low frequency vibrations, are easily encapsulated and light weight (allowing them to float), therefore they are considered the blue energy alternative for ocean wave energy harvesting [10].

This dissertation will start by an overview of TENGs in Chapter 2: from the triboelectric effect to the modified Maxwell's equations to account for triboelectricity, the fundamental operating modes and theoretical models of TENGs, and finally the most relevant results of published TENGs together with the challenges that motivate this work.

Afterwards, the methods of fabrication, characterization and analysis used will be detailed in Chapter 3, including the experimental setup, data analysis and materials characterization and deposition techniques.

Chapters 4 and 5 discuss the fabrication and performance of Poly(tetrafluoroethylene) foils for TENGs and the optimization of a promising TENG for ocean wave energy harvesting, respectively. To complement the latter investigation, multiphysics modelling and simulations were performed, whose results are presented in Chapter 6. Finally, Chapter 7 delivers the take away message and suggestions for future work.

Chapter 2

Triboelectric Nanogenerators

The first Triboelectric Nanogenerator (TENG) dates back to 2012 [1–3], being born to a team focused on piezoelectric generators. At that time, the scientific community learned how to take advantage of the static triboelectric effect to produce electrical energy, recognizing they had the potential to harvest energy “from human activities, rotating tires, ocean waves, mechanical vibration and more, with great applications in self-powered systems for personal electronics, environmental monitoring, medical science and even possibly large-scale power” (quoted from Fan, 2012 [1]).

A very important advantage of TENGs comparing to other technologies is their non expensiveness: firstly, the simplicity of the energy generation phenomena assures a low cost fabrication, and secondly, since almost any material acquires charge upon contact, the amount of materials available to be studied and proved to be adequate for effective energy generation is vast. Joining high power density (up to 500 W/m^2 [5]) and high energy conversion efficiency (up to 70% [11]), it is no surprise research in this topic is steadily increasing with a mean of 134 new papers every year for the last four years (according to the Web of Science database) and that the global market is predicted to increase 49% per year until 2025, reaching 113M€ in 2025 [12]. Until today, TENGs have proven their versatility and continue to offer new opportunities for application. One of the areas they excel at is ocean wave energy harvesting: traditional wave energy converters (WECs) still face many challenges, surpassed by TENGs due to the referred advantages plus their light weight, easy encapsulation (great features for incorporation on floating buoys) and ability to harvest irregular, low frequency excitations, such as ocean waves [4, 13]. For all this, ocean wave energy harvesting is a field of active ongoing research, with new nanogenerators being developed recently, with creative and effective designs [14, 15].

This chapter will start by explaining the origin of triboelectric charges, their nature and how they can be accounted for on the Maxwell's equations for electromagnetism. Then, the text will proceed to the induction of charges, while explaining the working mechanism of the four fundamental TENG geometries. Focusing on one of them, the contact-separation (CS) mode, the link between phenomena within the TENG and the external current will be established, and the power output described. Afterwards, two theoretical models of TENGs will be presented and compared in terms of voltage, current and power, paying attention to the internal and optimum resistances. Subsequently, the energy harvesting of ocean waves will be introduced, starting with a global description of waves and buoys, moving to representative TENGs and finally framing our device in this context.

2.1 Surface triboelectrification

Getting a static hair after taking off a piece of clothing or getting shocked when touching the car or a doorknob are events in life that we might be familiar with. In fact, the name *electron* derives from the greek *elektron*, or in english, "amber", from the observations of Thales of Miletus in 585 BC that amber attracted light objects, such as feathers, if it was previously rubbed with animal fur [16]. Not surprisingly, "triboelectric" means simply "rubbing amber". Nowadays, we translate this as an electric force of attraction between opposite charges, generated in the surfaces of the amber and the cloth through friction. Even though this report has more than 2500 years, today there is still no consensus in the scientific community about the processes that lead to surface electrification.

First of all, the mechanisms of charge transfer differ if they occur between metals, a metal and an insulator or two dielectrics [17, 18]. When two metals come into contact, they will exchange electrons so that their Fermi levels (meaning, their chemical potential at $T = 0K$) coincide, in order to minimize the electrons energy. Since each metal has a different work function (ϕ_1 and ϕ_2), a contact potential, named Volta potential, will arise as can be seen in Fig. 2.1.a, measurable only by Kelvin Probe Microscopy [18]. The amount of transferred charge is proportional to the contact potential by a specific capacitance and is limited by the attainment of the Fermi levels equilibrium, therefore rubbing the metals longer or harder does not increase it significantly [17]. However, in good insulators, charge has very low mobility so it is able to accumulate in time at the specific sites of contact [17]. Also, dependencies in the duration, type (rubbing, touching, single

or repeated contact) and speed of contact were found [17, 19]. For tribocharging involving insulators, achieving valid conclusions revealed to be more challenging. Inconsistent laboratory conditions, low reliability of experimental results, the complexity introduced by variable surface morphology, the vast collection of materials with different properties that exhibit contact electrification, the rareness of the charge transfer events (1 charge per 100000 atoms) and insufficient characterization of surface states of dielectrics [18–21] are some of the reasons why there is no convergence in the scientific understanding of triboelectrification - and most certainly there is no single process to it, but instead a combination of phenomena. In fact, two pieces of the same material were found to be charged when brought into contact - implying that no intrinsic property of the material can be solely responsible for contact electrification [22]. It is thus believed that electrification can occur due to a combination of transference of ions, bits of material and electrons, with some pairs of materials exhibiting a dominant mechanism [18, 21–23]. Here we will focus on dielectric surface charging due to electron transfer [20, 24, 25], presented in two different ways: the surface states model [17] and through a new approach centered on the overlapping of electron orbitals of the contacting atoms [24].

Let us start with the surface states discussion. Little new information about this model was found in literature, so this paragraph is based in an article solely about contact electrification by Lowell that dates back to 1980 [17], a recurrent reference on the topic, even on recent papers [18, 19, 22, 23]. Metals have Fermi levels around 4 eV under the vacuum level, while insulator bandgaps are situated between 1 eV and 8 eV under that same reference. After the observations of metal-insulator contact charging, it was postulated the existence of some unoccupied states laying on the insulator bandgap [17], as can be seen in Fig. 2.1.b-c (dashed line). Although there is not a systematic explanation of these midgap states, it is known they result from perturbations in the electrostatic potential of the periodic atomic lattice of materials [17, 20]. Hence, these states depend on the type of bonding: in covalent insulators, interactions between the molecules of the solid can create variations in the interatomic spacing (called intrinsic defects), therefore perturbing the potential; in polymers, the perturbations come from chain folding and branching, cavities and entanglements, unsaturated bonds, presence of free radicals or the incorporation of carbonyl groups and molecular oxygen [17] (these last called extrinsic defects). On another hand, the finitude of the materials periodic lattice is in itself a perturbation, and the bonding of impurities (such as ions) to certain surface regions also modifies the periodic

potential. Hence, new energy levels, called surface states, become available only at those sites. These surface states can have energies that fall on the bandgap of the bulk material and represent localized, trapping states. Some authors admit the existence of "bulk midgap states near surface" [26], but the designation that currently prevails is surface states [17, 20].

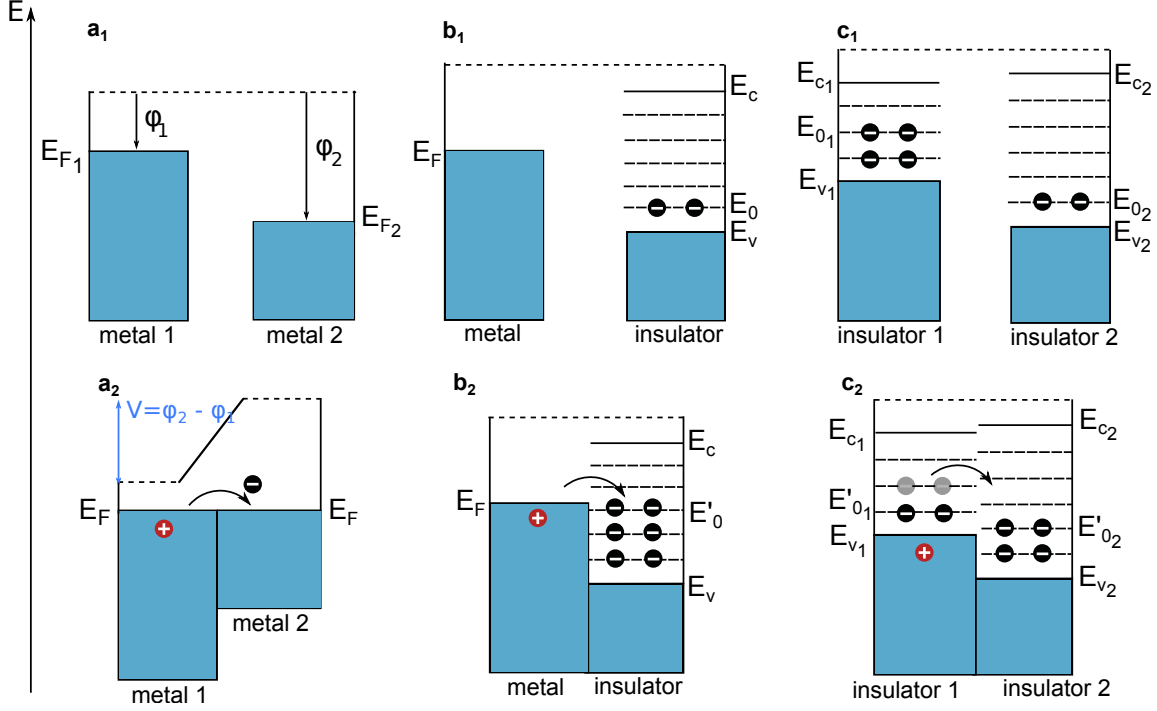


FIGURE 2.1: Schematic representation of the mechanism of contact electrification for (a) metal-metal (b) metal-insulator (c) insulator-insulator contact. The subscript 1 stands for before contact and images with subscript 2 represent the contact plus its effect of leaving one of the material positively charged (and the other negatively charged, not represented for simplicity)

But how do surface states relate to charge transfer? Between the valence and the conduction band of insulators, it can be defined a "neutral level of surface states" corresponding to the energy of the last occupied surface state E_0 , that serves as a guide for charge transfer [21]. From these definition there can be an effective or surface work function, analogous to that of metals, between the vacuum or outer potential and this neutral level. This way, charge would be transferred from the lowest to the highest surface work function material, similarly to what happens between metals. Experimentally, most insulators were found to charge negatively against metals [25], therefore it is plausible that in metal-insulator contact, electrons move from the metal to the unoccupied surface states on the insulator that are lower in energy than the metal Fermi level, that is, if $E_F > E_0$. Between

insulators, the reasoning is roughly the same. As represented in Fig. 2.1.c, electrons hop from occupied surface states in insulator 1 to lower unoccupied surface states of insulator 2 while in contact, that is, if $E_{0_1} > E_{0_2}$ [17, 20].

These mechanisms were recently supported by Kelvin Probe Force Microscopy (KPFM) experiments studying the influence of temperature [20, 24], and using a TENG as a measurement tool, studying the influence of incident light on the triboelectric layers [20, 27]. It was observed for metal-insulator contact that increasing the temperature of the metal will allow for states above the Fermi level to be occupied, injecting more negative charge on the insulator than with the metal at room temperature and even if $E_F < E_0$ [24]. Additionally, this same study shows that the generated surface charge decreases abruptly at very high temperatures, due to thermionic emission. Finally, by irradiating charged dielectrics in the wavelength range $[200, 400]nm$, the researchers found that trapped electrons can be released from the surface above a specific wavelength of incident light. This points to the existence of electrons trapped in surface states that can be excited into free electrons if provided with energy above a threshold value [20, 27].

However, there are materials whose electronic structure is not well described, neither from solid state band theory, nor from molecular orbitals, such as wood, animal fur and human hair, and still exhibit contact electrification [20]. Recently, a new model that ambitions to describe contact electrification in a general way was developed from KPFM observations [24]. Triboelectrification was detected between a KPFM platinum tip in tapping mode and insulators only when the tip entered the repulsive region of the sample surface [28]. This means electron transfer occurred only when the distance between the tip and the sample was smaller than the interatomic distance of the insulator [20]. Although tunneling was not excluded as a possible charge transfer process, a novel process of contact electrification at the atomic level was proposed [24], as shown in Fig. 2.2. According to this description, the contacting mechanical force merges the well potentials that confine the electrons to each atom, overlapping the electron clouds (electron wavefunctions) hence modifying the probability density function of electrons, allowing the transition of electrons between clouds of the material A and B (see Fig. 2.2.a₂). Considering that for each potential well there are well defined electron states, electrons will occupy the available states of the lowest energies. When the materials are separated (see Fig. 2.2.a₃), electrons can flow back depending on temperature (see Fig. 2.2.a₄), but after a minimum separation (estimated by Lowell [17] to be approximately 10 Å), charge backflow decays

to zero.

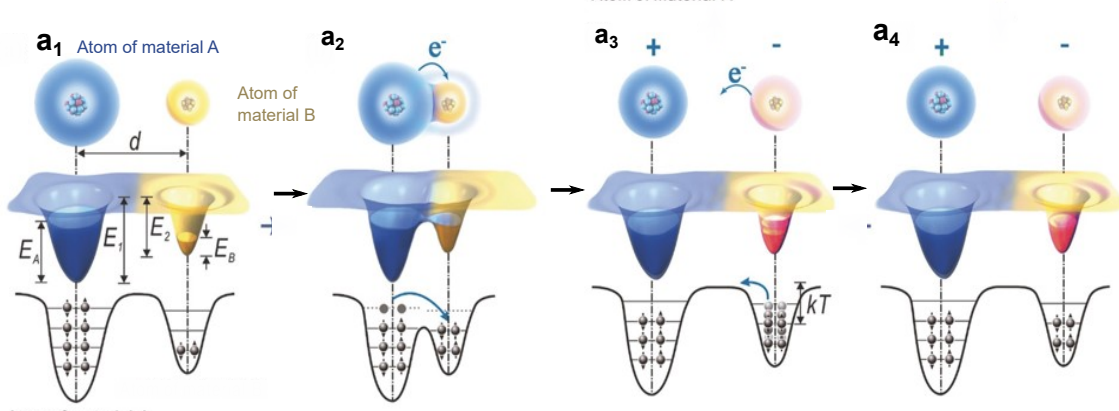


FIGURE 2.2: Contact electrification model at atomic level. Image adapted from [24].

In spite of all the debate on the nature and origin of contact electrification, some consensus exists on ranking materials according to their general behaviour of charging positively or negatively. This empirical arrangement is called the triboelectric series (see Figs. 2.3 and 2.4). However, different experimental and material conditions, for instance humidity, temperature, surface morphology and strain [18, 25], (that modifies the electronic structure, since crystal deformation leads to a change in the electrostatic potential of the metal [29]), have produced different results. It should be noted as well that the sign of the generated triboelectric charges is always relative to the counterpart material. Recently, a quantitative triboelectric series was created using a TENG as a measurement tool [25]. A wide variety of insulators was tested on mercury at room temperature, since its liquid phase has high adaptability to the tested material surface [25] and because the metal-insulator contact is better understood than the insulator-insulator one. All measurements were performed in a well controlled environment (fixed temperature, humidity and ambient and contact pressure) inside a glove box. Most insulators tested to create this triboelectric series, represented in Fig. 2.3, acquired negative charge up to 10^{-4} $\mu\text{C}/\text{m}^2$. It should be stressed that triboelectric charge increases with the number of contacts until it reaches a saturation value (for over 100 cycles), the one taken into account for the construction of the quantitative triboelectric series [25, 30].

It is possible to find insulators charging positively against mercury, as demonstrated by another work from the same group [30] for inorganic insulators (see Fig. 2.4). Other materials not included in the two triboelectric materials presented so far, but worthy of note, are human skin, hair and animal fur, placed above the mineral Mica on the series of Fig. 2.4, and natural fibers such as wool, silk, paper and cotton, placed under the Mica

[18, 31]. Although irregularities can be found as explained above, the more set apart two materials are in the triboelectric series, the more different their neutral levels based on the surface states model are, therefore the higher the triboelectric charge generated on contact.

Different strategies are employed to increase the generated triboelectric charges, from whose we distinguish three categories: micro/nanostructuring, material engineering and electrical. Laser patterning [32, 33], reactive ion etching [34], lithography [2, 35] and many others [7] have been used to create rugosities on the surface of triboelectric materials, increasing the contact area, hence the generation of more surface charges. On another hand, incorporating fluorine (note that fluorinated compounds have a high electron affinity and for that they are usually situated on the extremity of the triboelectric series [36]), doping with metalorganic compounds through Sequential Infiltration Synthesis [37], inserting extra charged ions or molecules [38] and doping the triboelectric layers with nanoparticles to change the dielectric properties (for instance, increasing the electric permittivity [39]) are some of the material engineering methods [7]. Finally, using different power management strategies it is possible to promote a fast and more effective charge accumulation [40], or perform charge pumping, transferring charges from an auxiliary TENG to the main TENG [41].

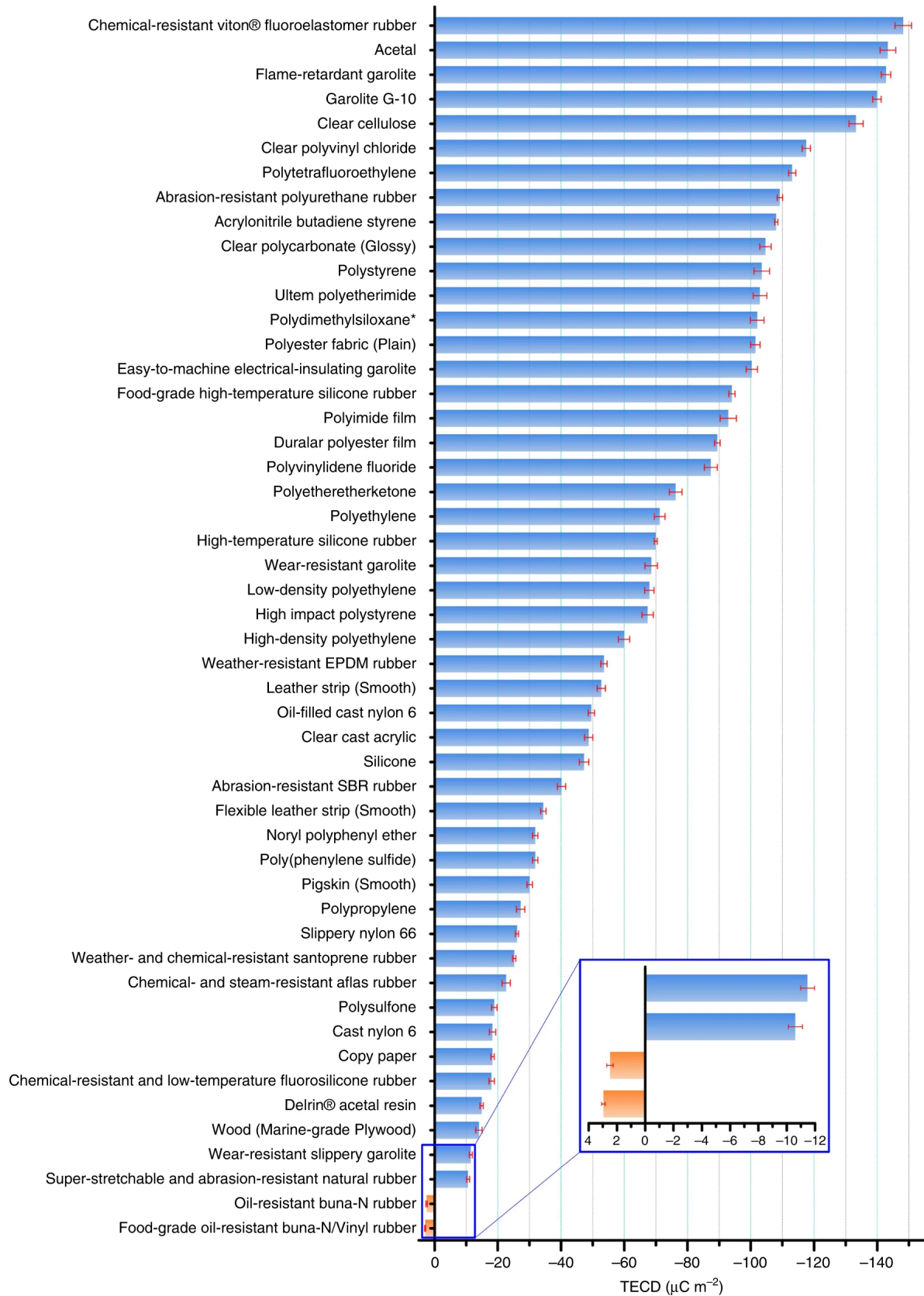


FIGURE 2.3: Quantitative triboelectric series of materials against liquid mercury [25].

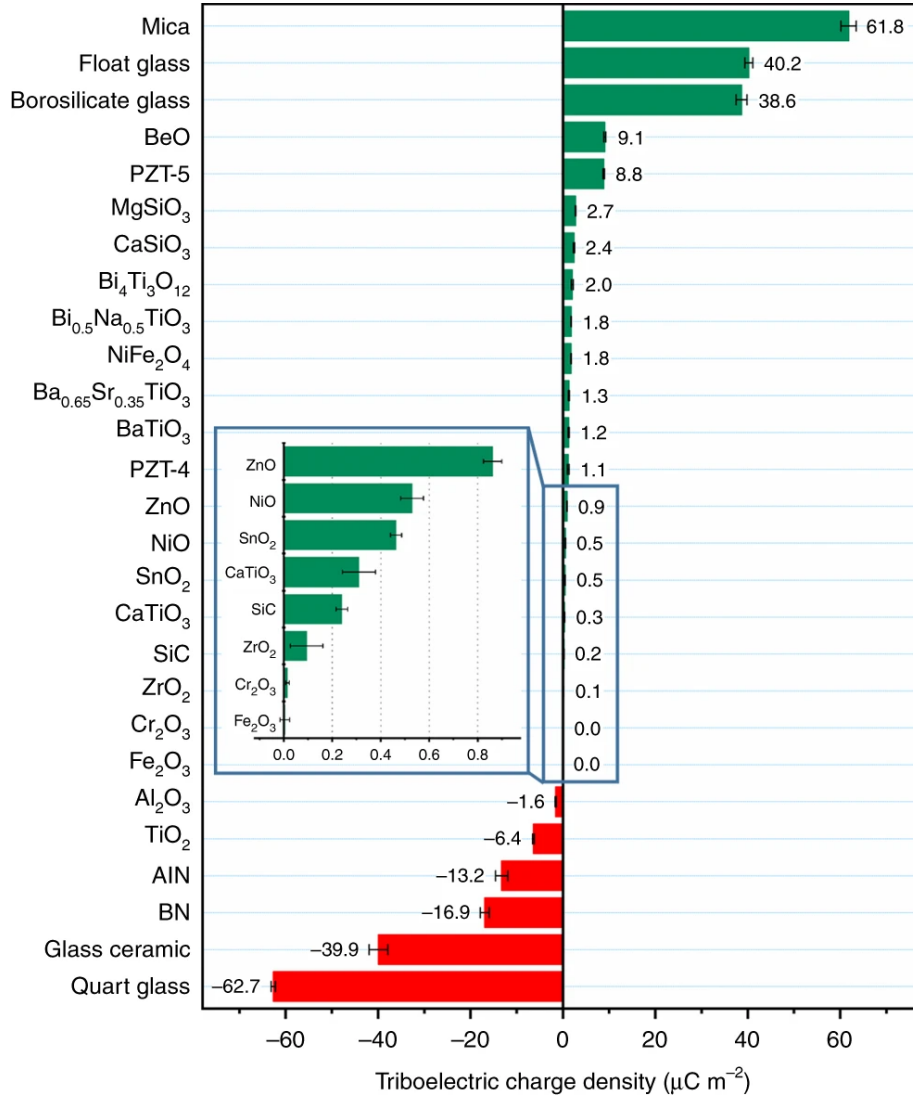


FIGURE 2.4: a) Quantitative triboelectric series for a set of inorganic materials [30].

2.2 From the Wang's term to output power

Now that the origin of triboelectric charges was presented, this section will focus on the induced charges on the electrodes and their relation to output power.

From electrostatics, it is known that an electric polarization field $\mathbf{P}$ arises on insulators in the presence of an external electric field. The electric force at the atomic level slightly displaces the electronic clouds relative to their respective nucleus, creating atomic-sized electric dipole moments, whose volume density corresponds to $\mathbf{P}$. On the boundaries of a finite material, or due to non-uniformities of $\mathbf{P}$, this effect results in bound charges,

at the surface ($\sigma_b = \mathbf{P} \cdot \hat{\mathbf{n}}$) or in the bulk material ($\rho_b = -\nabla \cdot \mathbf{P}$), respectively, that are irremovable, hence their designation [42].

Nonetheless, the triboelectric surface charges are not a consequence of an external electric field, and therefore, cannot be accounted on the $\mathbf{P}$ field [43]. A new polarization term $\mathbf{P}_s$ was introduced by Zhong Lin Wang in 2017 [10] to represent the effect of charges mechanically and strain induced (respectively important in triboelectric and piezoelectric effects), therefore independent of any other electric fields. The piezoelectric effect will be neglected since this thesis regards triboelectric materials only. This new polarization can be accounted for in the equations of the total charge on the system, where the subscript f accounts for free charges:

$$\sigma = \sigma_f + \sigma_b + \mathbf{P}_s \cdot \hat{\mathbf{n}} \quad (2.1) \quad \rho = \rho_f + \rho_b - \nabla \cdot \mathbf{P}_s. \quad (2.2)$$

Consequently, from the Gauss's law applied to the total charges on the system $\nabla \cdot \mathbf{E} = \frac{\rho}{\epsilon_0}$, and knowing that the flux of the electric displacement field through a closed surface equals the total free charges on the system (in differential form $\nabla \cdot \mathbf{D} = \rho_f$) one calculates the electric displacement field in the presence of triboelectric charges as [10]:

$$\epsilon_0 \mathbf{E} + \mathbf{P} + \mathbf{P}_s = \mathbf{D} \iff \mathbf{D} = \mathbf{D}' + \mathbf{P}_s. \quad (2.3)$$

Although Maxwell's equations hold true for this modified electric displacement field, to evidence the introduction of $\mathbf{P}_s$ in the electric displacement field, a full description can be made as function of the electric displacement field before the introduction of triboelectricity $\mathbf{D}' = \epsilon_0 \mathbf{E} + \mathbf{P}$. Now, if one calls ρ' the charge associated with $\mathbf{D}'$:

$$\rho' = \nabla \cdot \mathbf{D}' = \nabla \cdot \mathbf{D} - \nabla \cdot \mathbf{P}_s \quad (2.4)$$

$$= \rho_f - \nabla \cdot \mathbf{P}_s, \quad (2.5)$$

accounting for free and triboelectric charges, so that the actual displacement field $\mathbf{D}$ continues to account for free charges only.

From Eq. 2.5 and the continuity equation $\frac{\partial \rho'}{\partial t} + \nabla \cdot \mathbf{J}' = 0$, it's possible to find the current $\mathbf{J}'$ associated with ρ' :

$$\begin{aligned}
\frac{\partial \rho'}{\partial t} &= \frac{\partial \rho_f}{\partial t} - \nabla \cdot \frac{\partial \mathbf{P}_s}{\partial t} \\
&= \nabla \cdot \left(-\mathbf{J}_f - \frac{\partial \mathbf{P}_s}{\partial t} \right) \\
&= -\nabla \cdot \mathbf{J}' \implies \mathbf{J}' = \mathbf{J}_f + \frac{\partial \mathbf{P}_s}{\partial t}
\end{aligned}$$

This way, the new set of modified Maxwell's equations which rule currents, charges and electromagnetic fields in TENGs becomes [43]:

$$\begin{cases} \nabla \cdot \mathbf{D}' = \rho' & (2.6a) \\ \nabla \cdot \mathbf{B} = 0 & (2.6b) \\ \nabla \times \mathbf{E} = -\frac{\partial \mathbf{B}}{\partial t} & (2.6c) \\ \nabla \times \mathbf{H} = \mathbf{J}' + \frac{\partial \mathbf{D}'}{\partial t}, & (2.6d) \end{cases}$$

where $\mathbf{B}$ is the magnetic field and $\mathbf{H}$ is an auxiliary field, related to the previous as $\mathbf{H} = \left(\frac{1}{\mu_0} \mathbf{B} - \mathbf{M} \right)$.

Rewriting the last Maxwell Eq. (2.6d), one can stress the nature of the existing current densities on the system, free and displacement:

$$\nabla \times \mathbf{H} = \mathbf{J}_f + \underbrace{\frac{\partial \mathbf{P}_s}{\partial t} + \frac{\partial \mathbf{D}'}{\partial t}}_{\mathbf{J}_D} \quad (2.7)$$

where $\frac{\partial \mathbf{P}_s}{\partial t}$ is called the Wang's term, a new contribution to the displacement current.

In 1886, when only electric currents were known to create magnetic fields, Maxwell [44] introduced the displacement current density to account for time-varying electric fields as another source of magnetic fields, creating the path for the description of electromagnetic waves [45]. On the other hand, the Wang's term represents yet another contribution to the displacement current, this time due to mechanically induced charges. Consequently, any magnetic field is created either by free currents, either by displacement currents [46], that comprise, more than time-varying electric fields (in vacuum or polarizable media) and their associated electric polarization fields when applicable, also time varying polarization fields, mechanically and strain originated.

In order to create a TENG device, not only surface charges must be generated, but electrodes with free charges must be present, to be influenced by the electrostatic potential

created by the triboelectric charges. The simplest geometric arrangement of these layers is the vertical contact-separation (CS) mode, composed of two electrodes and two triboelectric layers as represented in Fig. 2.5.a. Also for the collection of vertical movement, but with only one electrode and triboelectric layer, there is the single-electrode mode (Fig. 2.5.b). Another two fundamental modes exist, that rely on lateral movement: the contact or lateral sliding mode (Fig. 2.5.c), analogous to the CS mode, and finally the freestanding layer mode (Fig. 2.5.d), that uses two electrodes on one side facing a single triboelectric layer [47–49]. Although there are countless geometries built and experimentally verified as viable energy generators that may not strictly follow these morphologies due to being adapted to harvest a specific mechanical excitation, most of them are grounded on these four operating modes.

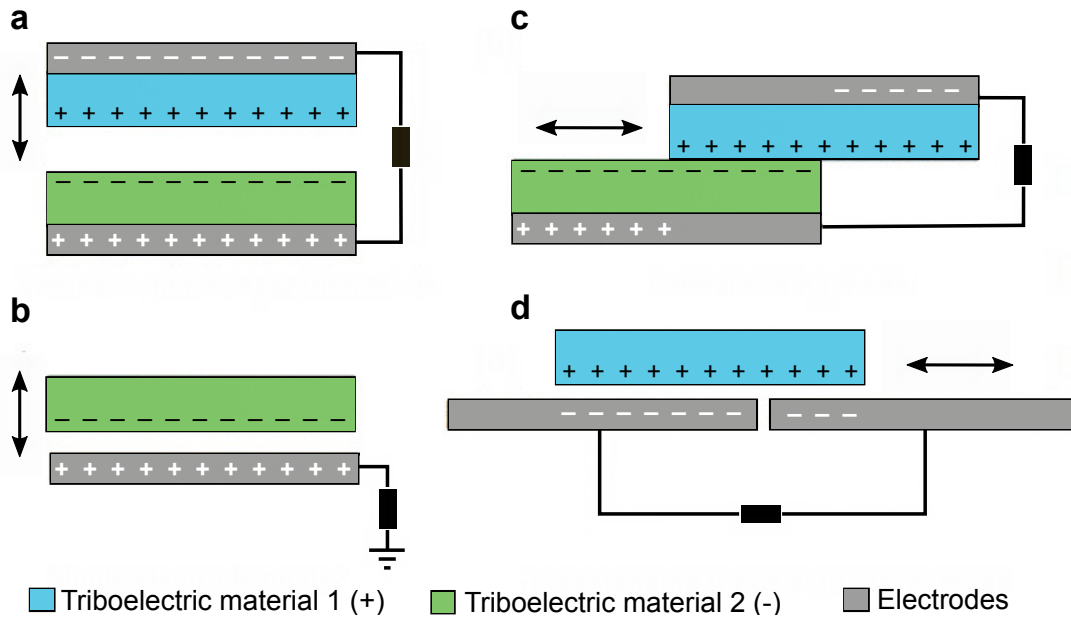


FIGURE 2.5: Four fundamental modes of TENGs: a) Contact-separation; b) Single electrode; c) Sliding; d) Freestanding. Adapted from [50]

After some cycles rubbing/pressing the triboelectric layers with opposite polarity together, the surface charge density reaches its steady state value as referred in section 2.1. The working principle of these modes is very similar: the relative displacement of the triboelectrically charged layers (in the case of the single electrode or freestanding layer mode, one of those layers is also a metal electrode) modifies the electrostatic potential spatial distribution, hence a time varying charge is induced on the electrode(s), producing an electric current [49]. Some features should be further referred (for the short circuit condition): in the lateral sliding mode, since the triboelectric materials are always in contact,

the space between positive and negative triboelectric charges is negligible in comparison with the lateral sliding distance. Therefore, when the area of contact is maximum, no charge is induced due to the charge screening effect of the contacting surfaces. The same occurs for the CS mode, when the two triboelectric charged surfaces are pressed together and practically coincide. It is worth noting that the single electrode mode has the advantage of possessing a triboelectric layer without an attached electrode, which constitutes an advantage for many applications [48, 50]. A similar benefit can be appointed to the freestanding layer mode, whose electrodes are on the same side, and the dielectric layer is free from electrical connections. Moreover, since in this mode there is no direct contact between the layers, the materials undergo no degradation [48].

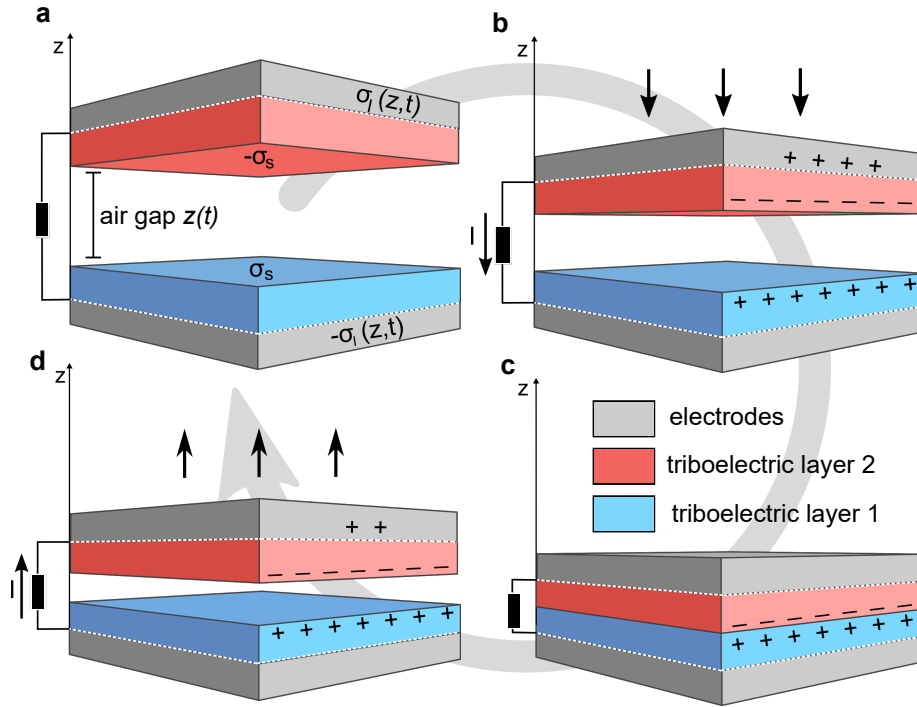


FIGURE 2.6: Vertical contact separation mode cycle. a) Initial position with the layers separated; b-d) The position of the two top layers relative to the bottom layers (air gap) is a periodic function of time $z(t)$.

This dissertation will be focused on a device based on the CS mode, whose operating cycle is depicted in Fig. 2.6. In this arrangement, varying the distance between the triboelectric layers with surface charge $\pm\sigma_s$ causes the induced electrostatic charges on the electrodes to vary accordingly, therefore we write $\sigma_I(z, t)$ (see Fig. 2.6.a). If charges are allowed to flow freely (small load impedance), at the starting position (maximum separation), each electrode will be charged with opposite polarity of the attached triboelectric layer, charge whose value will depend on the separation distance and the load [49]. If the

distance $z(t)$ does not change, then σ_I is at an equilibrium value and no current will be generated, hence the need of an external mechanical excitation. When the layers approach each other (Fig. 2.6.b), the top electrode is subjected to a different electric field value and the previous electrostatic equilibrium is disrupted. As a consequence, positive charges are displaced to the bottom electrode, or in other words, the value of the induced charge starts to decrease, and a current is generated. In Fig. 2.6.c, the triboelectric surfaces are in contact, screening one another, hence the induced charge is zero. When they are separated (Fig. 2.6.d), the top electrode starts to get positively charged again, as a current of inverse polarity flows through the external load.

Going back to the beginning of this section, one may ask how is the displacement current connected to this "current", the output current, that flows through the external load Z . To better understand this relation, let us consider Fig. 2.7, that represents the simplest geometry of vertical contact-separation of the triboelectric layers and two electrical contacts. The charge time derivative induced on the electrodes $Q(t) = A\sigma_I(t)$ is the current on the load [43], where A is the area of the electrodes, assuming an uniform spatial distribution of the induced surface charges.

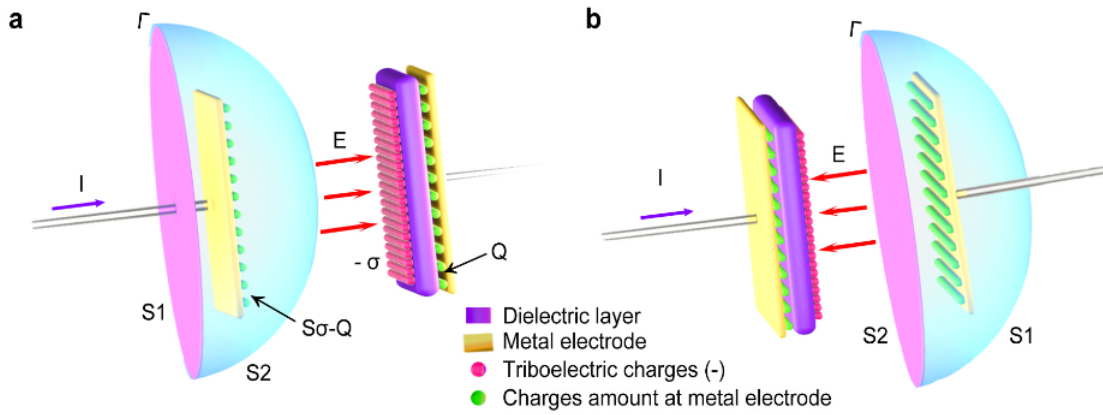


FIGURE 2.7: Illustration of a CS TENG and two different surfaces, S1 and S2, bounded by the same path Γ . **a** and **b** show that S1 and S2 can interchange shapes, but S1 is always the surface for which the flux of J_f is nonzero, and the equivalent for S2 and J_D [46].

There is no doubt there exists a magnetic field around the wire (with origin in both free and displacement currents), with which the path Γ is chosen to be collinear with, as translated by the Maxwell Eq. (2.6d) in integral form $\oint_{\Gamma} \mathbf{B} \cdot d\mathbf{l} = \iint_S (\mathbf{J}_f + \mathbf{J}_D) \cdot d\mathbf{S}$; here S is any surface bounded by Γ . We can analyze free and displacement currents separately by their flux through two different surfaces, S1 and S2, respectively (see Fig. 2.7), but each bounded by that same path Γ . The flux of $\mathbf{J}_f$ is nonzero only for surface S1, and the flux of

$\mathbf{J}_D$ is only nonzero through surface S_2 (since the electric field is nonzero only in between the metal plates). This means that, since they both contribute to the same magnetic field, if the flux of $\mathbf{J}_f$ through S_1 is the electric current on the external circuit, then the flux of $\mathbf{J}_D$ through S_2 must take the same value [43]:

$$\iint_{S_2} \mathbf{J}_D \cdot d\mathbf{S} = \iint_{S_1} \mathbf{J}_f \cdot d\mathbf{S} = I \iff I_D = \frac{\partial Q}{\partial t}. \quad (2.8)$$

Recognizing at last that it is the displacement current inside a nanogenerator that drives the output current in energy harvesting systems which rely on a mechanical induced polarization, such as TENGs [10, 43, 46], forming a closed, complete circuit from the transducer to the load [51].

It is now possible to establish an equation for the TENG power transfer, from the induced surface charge density. Considering any TENG geometry and Ohm's Law, the instantaneous power provided at the load is [51]:

$$P(t) = ZA \left\{ \frac{\partial \sigma_I[z(t)]}{\partial t} \right\}^2. \quad (2.9)$$

In order to determine σ_I for each TENG geometry, a closer look to the spatial electric potential distribution is needed, considering that the potential at the load is a function of the electric field integral over a path connecting the two electrodes (the potential difference between them):

$$V = - \int \mathbf{E} \cdot d\mathbf{z} = ZA \frac{\partial \sigma_I[z(t)]}{\partial t}. \quad (2.10)$$

As it will become more clear in the following section, the electric potential will be different for each geometry, surface charge, dielectric constant and thicknesses of the triboelectric layers, modifying in its turn the induced surface charge density according to Eq. (2.10). Therefore, the modification of material properties as well as the movement characteristics are extremely relevant to maximize the delivered power. In fact, determining the electric potential for a specific geometry plus recognizing the displacement current as the motif for free current in Eq. (2.8) constitutes a first order differential equation in $\sigma_I(t)$, adding an initial condition [usually $\sigma_I(0) = 0$], completely determines the electrical output of any TENG [51].

2.3 Theoretical models

The theoretical models of TENGs are the fundamental description of their working principle. Each model provides a different Equation for the electric potential, according to the assumptions it makes, that can be plugged in Eq. (2.10), allowing us to predict the electrical power output for a set of parameters.

The first TENG model assumed the charged layers were infinite [2], since the thickness of the layers and their relative displacement (μm - mm) is typically at least one order of magnitude smaller than their typical length (cm - dm). From the construction of the equivalent circuit model and its association with this electric potential of infinite planes was born the capacitive model (CA model) [47, 52]. However, a more rigorous finite charged layers model, the Distance Dependent Electric Field model (DDEF model) has been recently explored and compared with the previous one [43] and with experimental results [53].

Before dwelling into each model, the typical current, voltage and power (IVP) response of TENGs is presented. A contact-separation generator with Polytetrafluoroethylene (PTFE) as triboelectric 1 and Nylon as triboelectric 2 (see Fig. 2.6) was simulated using the CA model for simplicity, with the parameters shown in Table 2.1.

Parameter	Value	Parameter	Value
L	4 cm	W	2.5 cm
σ_S	50 μC	Area	10 cm^2
ϵ_{r_1}	2.75	ϵ_{r_2}	4
d_1	100 μm	d_2	100 μm
v	4 m/s	A_z	500 μm
T	$\frac{A_z 2\pi}{v}$ s	Function $z(t)$	$500 + A_z \sin(\frac{v}{A_z} t) \mu\text{m}$

TABLE 2.1: Simulation parameters of the typical IVP curves represented in Fig. 2.8, where, of the triboelectric layers: L and W are the length and width, σ_S is the surface charge density, ϵ_{r_1} and ϵ_{r_2} are the relative electric permittivities, d_1 and d_2 the thicknesses.

As explained in section 2.2, in the CS mode the induced surface charge varies between zero (when the two triboelectric layers contact) and a certain value, as represented in Fig. 2.8.a, lower than the triboelectric charge density. In fact, the quotient between the maximum induced surface charge (the charge transferred on short circuit) and the triboelectric charge is called the charge transfer efficiency, that depends on the structure of the TENG [54]: $\eta_{CT} = Q_{SC} / Q_{tribo}$. The current on a resistive load is depicted in Fig. 2.8.b. Being the

derivative function of the induced surface charge density, one can see its peaks, signaled in red, correspond to the rapid variation of σ_I close to points where $\sigma_I = 0$, that is, the zero distance between layers $z = 0$ (see Figs. 2.8.a,c). From the peak values of current and voltage, one can build the IVP curves for different load values, as shown in Fig. 2.8.d.

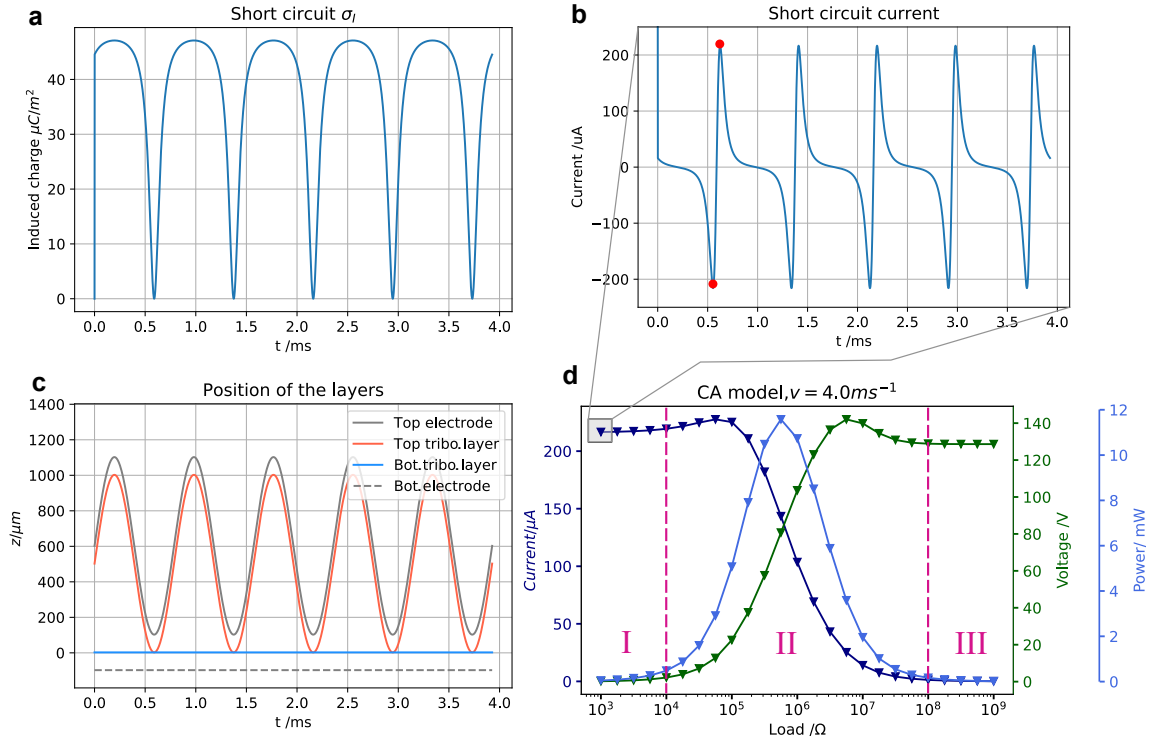


FIGURE 2.8: a) The induced charge density σ_I and I for the lowest resistance calculated ($10^3 \Omega$, representative of the short circuit condition) and b) correspondent current. The peaks are a direct response of the pressing/releasing cycle. c) The vertical position of the layers on time. d) I, V and P curves evidencing a maximum power point and the regions I,II,III. This graph is built from the I and V peak values, represented in red in a).

The I, V and P curves in Fig. 2.8 are usually subdivided into three regions [48]. The region I corresponds to small resistances, in which the peak current is almost constant and equal to the short circuit value. In region II is found the maximum power point, where current falls abruptly towards zero, while voltage follows the inverse trend and increases rapidly. In region III, for high resistance values, current reaches a low, steady value, while voltage is reaching for the open circuit value. This classification is not strict in terms of resistance delimitation, since the optimum resistance varies with the geometry of the TENG [52]. It should be noted that this IVP behaviour imposes the existence of a maximum power point for all TENGs, correspondent to an optimum resistance lying in the second region.

2.3.1 DDEF model

This model considers the electric potential distribution of finite-sized charged planes to solve Eq. (2.10). Due to their finitude, the electric field will be a function of (x, y, z) , hence on the time varying distance along the z direction between triboelectric layers and electrodes; therefore, it is called the Distance Dependent Electric Field (DDEF) model. Let us consider N finite-sized layers of charge of surface charge density σ_i , parallel to one another and positioned along the z -axis at the level z_i (valid for the CS mode), width W and length L , as in Fig. 2.6. Then, the electric field becomes [43]:

$$\mathbf{E}(x, y, z) = \sum_{i=1}^N \frac{\sigma_i}{4\pi\epsilon(z)} \int_{-L/2}^{L/2} \int_{-W/2}^{W/2} \frac{(x - x', y - y', z - z_i) dx' dy'}{[(x - x')^2 + (y - y')^2 + (z - z_i)^2]^{\frac{3}{2}}}, \quad (2.11)$$

where x', y' are the integration variables on each plane of charge. The CS mode has a minimum of 2 triboelectrically charged layers (with $\pm\sigma_T$) and 2 induced charged surfaces (with $\pm\sigma_I$), hence $N = 4$ and therefore $\epsilon(z)$ is defined as a step function in the region of interest $z \in [z_1, z_4]$:

$$\epsilon(z) = \begin{cases} \epsilon_{T1}, & z_1 < z < z_2 \\ \epsilon_{air}, & z_2 < z < z_3 \\ \epsilon_{T2}, & z_3 < z < z_4 \end{cases} \quad (2.12)$$

Being each surface at z_i an equipotential surface, in order to calculate the electric potential difference between the two electrode surfaces one can trace any path. If a straight path along the z -axis is chosen, one takes advantage of symmetry in the x and y directions, and only the electric field along the z -axis needs to be calculated:

$$E_z(0, 0, z) = \sum_{i=1}^N \frac{\sigma_i}{4\pi\epsilon(z)} \int_{-L/2}^{L/2} \int_{-W/2}^{W/2} \frac{(z - z_i) dx' dy'}{[x'^2 + y'^2 + (z - z_i)^2]^{\frac{3}{2}}}. \quad (2.13)$$

Computing the double integral in Eq. (2.13) as the function $f(z)$ [55]:

$$f(z) = \arctan \left(\frac{\frac{L}{W}}{2 \frac{z}{W} \sqrt{4 \left(\frac{z}{W} \right)^2 + \left(\frac{L}{W} \right)^2 + 1}} \right), \quad (2.14)$$

and evaluating f at each charged surface $(z - z_i)$, the electric field E_z becomes:

$$E_z(0,0,z) = \sum_{i=1}^N \frac{\sigma_i}{4\pi\epsilon(z)} f(z - z_i). \quad (2.15)$$

From this equation, the electric potential is written:

$$\begin{aligned} V &= - \int_{z_1}^{z_4} E_z dz \\ &= \sum_{i=1}^N \frac{\sigma_i}{4\pi} \left[\frac{1}{\epsilon_{T1}} \int_{z_1}^{z_2} f(z - z_i) dz + \frac{1}{\epsilon_{air}} \int_{z_2}^{z_3} f(z - z_i) dz + \frac{1}{\epsilon_{T2}} \int_{z_3}^{z_4} f(z - z_i) dz \right]. \end{aligned} \quad (2.16)$$

This electric potential Eq. (2.16) can now be used to solve the differential Eq. (2.10) for σ_I , in order to determine the power output for the CS mode with Eq. 2.9. Note that this value must be calculated for each instant, since the distance between triboelectric layers $z(t)$ is a function of time.

2.3.2 CA model

If one assumes that the distance between the electrodes is much smaller than their lateral dimensions, the electric field in each dielectric region (triboelectric layers and air) can be obtained from the infinite charged planes electric field [10]:

$$\begin{cases} \mathbf{E}_1 = \frac{\sigma_I}{\epsilon_1} \hat{\mathbf{z}}, & \text{dielectric 1} \\ \mathbf{E}_0 = \frac{\sigma_I - \sigma_s}{\epsilon_0} \hat{\mathbf{z}}, & \text{air gap} \\ \mathbf{E}_2 = \frac{\sigma_I}{\epsilon_2} \hat{\mathbf{z}}, & \text{dielectric 2} \end{cases} \quad \begin{aligned} (2.17a) \\ (2.17b) \\ (2.17c) \end{aligned}$$

Therefore the electric potential becomes:

$$V = \sigma_I \left(\frac{d_1}{\epsilon_1} + \frac{d_2}{\epsilon_2} \right) + (\sigma_I - \sigma_s) \frac{z(t)}{\epsilon_0}, \quad (2.18)$$

where d_1, d_2 are the thicknesses of the dielectrics and $z(t)$ is the distance between triboelectric layers, equal to the air gap thickness. This equation is in fact an approximation to the more accurate electric potential from the DDEF model, the Eq. (2.16). However, it is worthy to note its simplicity comparatively to its counterpart from the DDEF model. For that reason, one can already plug Eq. (2.18) in Eq. (2.10):

$$ZA \frac{d\sigma_I(t)}{dt} - \sigma_I(t) \left(\frac{d_1}{\epsilon_1} + \frac{d_2}{\epsilon_2} + \frac{z}{\epsilon_0} \right) = \sigma_s \frac{z}{\epsilon_0}, \quad (2.19)$$

in order to explore the short circuit current analytically. If $V = ZA \frac{d\sigma_I(t)}{dt} = 0$, the solution for σ_I from Eq. (2.19) is straightforward and the short circuit current reads [10]:

$$I_{SC} = A\sigma_s \frac{dz(t)}{dt} \frac{d_1\epsilon_0/\epsilon_1 + d_2\epsilon_0/\epsilon_2}{[d_1\epsilon_0/\epsilon_1 + d_2\epsilon_0/\epsilon_2 + z(t)]^2}. \quad (2.20)$$

This result hints that the generated power depends not only on the material properties, load, and triboelectric charge, but also on the distance between layers at each instant $z(t)$ and the speed of the layers movement $\frac{dz(t)}{dt}$.

Tracing back to section 2.1, any TENG is composed of triboelectrically charged surfaces, insulated from the electrodes, plus the movement-induced charged planes [with transferred charges $Q(t) = A\sigma_I(t)$ as previously stated], the electrodes. These alone constitute a variable capacitor, contributing to the electric potential difference between electrodes with $-Q/C(z)$ [47]. On the other hand, even if no charge was transferred between the electrodes, as the ideal open circuit case, the triboelectrically charged surfaces would also contribute to the electric potential difference, corresponding to a variable voltage source $V_{OC}(z)$ [47, 52]. This leads to the well known "V-Q-x" relationship that relates directly to the equivalent circuit in Fig. 2.9:

$$V = -\frac{Q}{C(z)} + V_{OC}(z). \quad (2.21)$$

Since in the CS mode the movement is along only one axis, it was historically represented by x , but in fact to be coherent with the rest of the models here this direction will be denoted by z .

Comparing this equation to Eq. (2.18), it is possible to identify for the CS mode in particular:

$$\left\{ \begin{array}{l} C(z) = \frac{A}{d_1/\epsilon_1 + z/\epsilon_0 + d_2/\epsilon_2} \end{array} \right. \quad (2.22a)$$

$$\left\{ \begin{array}{l} V_{OC}(z) = \frac{\sigma_s z}{\epsilon_0} \end{array} \right. \quad (2.22b)$$

Or, as it is usually written [48]:

$$\left\{ \begin{array}{l} C(z) = \frac{\epsilon_0 A}{d_0 + z} \end{array} \right. \quad (2.23a)$$

$$\left\{ \begin{array}{l} V_{OC}(z) = \frac{\sigma_s z}{\epsilon_0}. \end{array} \right. \quad (2.23b)$$

where d_0 is the effective dielectric thickness given by $d_0 = \frac{d_1}{\epsilon_{r1}} + \frac{d_2}{\epsilon_{r2}}$. Note that if the electric potential from the DDEF model was substituted in Eq. (2.21), making these identifications would not be possible. Therefore, although the CA model is an approximation of the DDEF, its simplicity reveals useful in order to estimate the TENG behaviour.

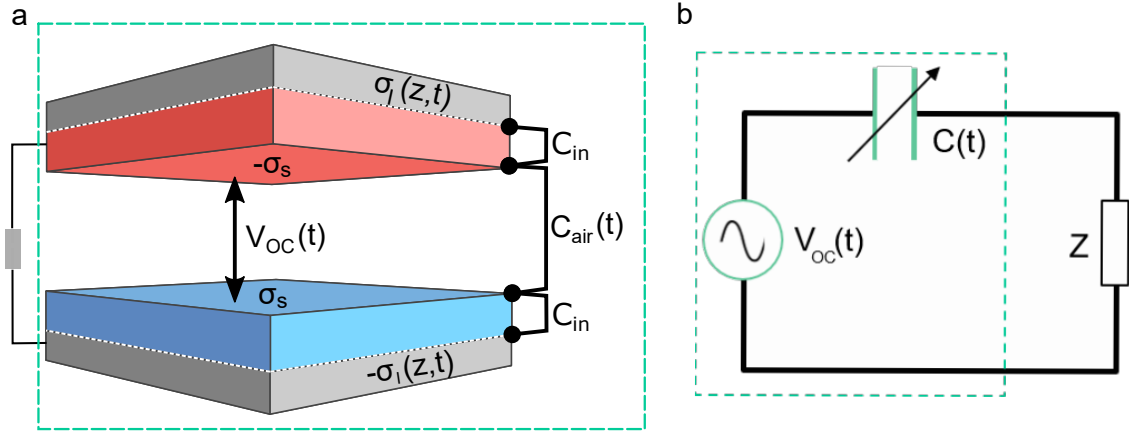


FIGURE 2.9: Inside the dashed line, connected to a generic impedance Z , there is: a) A visual representation of the TENG equivalent circuit, in dashed line. b) The TENG equivalent circuit. Adapted from [53].

It should be stressed that according to Eq. (2.23b), the open circuit voltage does not consist of symmetric positive and negative peaks in time as depicted in Fig. 2.8, but it is instead completely determined by the function $z(t)$. Nonetheless, for simplicity, the voltage response for resistances on region III is already considered open circuit voltage.

Concerning the capacitive term on Eq. (2.23a), its variable part comes only from the air gap that varies with time C_{air} , since the thicknesses of the other insulators are fixed. Hence, it is possible to subdivide the TENG capacitance in the fixed component C_{in} and a variable component C_{air} connected in series [43]:

$$C(z)^{-1} = \frac{1}{C_{in}} + \frac{1}{C_{air}(z)} \quad (2.24)$$

Making the definition of C_{air} and C_{in} :

$$C(z)^{-1} = \frac{d_0 + z}{\epsilon_0 A} \implies \begin{cases} \frac{1}{C_{in}} &= \frac{d_0}{A\epsilon_0} \\ \frac{1}{C(z)_{air}} &= \frac{z}{A\epsilon_0}. \end{cases} \quad (2.25)$$

If one desires to have a less variable capacitance, $1/C_{air} \ll 1/C_{in}$, the condition $z \ll d_0$ must be satisfied, that is, the air gap $z(t)$ must be much smaller than the thickness

of dielectrics. This condition is not always possible to fulfill, depending on the average force that promotes the contact between layers. On the other hand, the open circuit voltage depends on $z(t)$. Therefore, when designing a TENG a balance must be achieved between a less variable capacitance, useful for power management applications, or a higher maximum achievable potential difference, indicative of higher power.

Additionally, since any real capacitor presents some parasitic inductances and resistances, the TENG is no exception, and truncating the level of detail to a certain degree, an internal resistance can be found due to the insulation between the electrodes. This internal resistance is close to infinity [49], therefore when in parallel has a negligible contribution to the equivalent impedance. Hence, TENGs are most often described to behave as a pure capacitive impedance:

$$Z_{eq} = \left[\frac{1}{R_{int}} + sC \right]^{-1} \approx \frac{1}{sC}. \quad (2.26)$$

In order to demonstrate that a TENG is capable of delivering useful power, a resistor R whose job is to dissipate power is always used as a load. In that case, the circuit behaves as a high pass filter with cutoff frequency $f = \frac{1}{2\pi RC}$:

$$V_{out}(s) = \frac{R}{R + \frac{1}{sC}} V_{in}(s). \quad (2.27)$$

Considering that the capacitance varies over a contact/separation cycle, and the frequency of the movement depends on the regularity or irregularity of the vibrations that are being harvested, tuning the value of the resistor may seem difficult. At first glance, increasing R boundlessly would reduce the cutoff frequency well below operation frequencies. However, reducing the attenuation of the output voltage signal is not as important as maximizing the power delivered at the load. Therefore, one can write:

$$P = \frac{[V_{out}(s)]^2}{R} = \frac{R}{(R + \frac{1}{sC})^2} [V_{in}(s)]^2 \quad (2.28)$$

and thus:

$$\frac{\partial P}{\partial R} = 0 \xLeftrightarrow{s=jw} R = \frac{1}{wC} \iff R = \frac{d_0 + z}{Aw\epsilon_0}, \quad (2.29)$$

so that the optimum resistance is equal to the absolute value of the internal impedance, although capacitive, of the TENG. Another result was obtained by Niu *et al* [52], where

the optimum resistance was derived to be, for the CS mode, uniform approaching velocity v and maximum separation between layers z_{max} :

$$R_{opt} = \frac{(d_0 + z_{max})^2}{Av\epsilon_0}. \quad (2.30)$$

Considering the relation between contact velocity and angular velocity of a sinusoidal motion (hence periodic output characterized by w), from $z(t) = z_{max} \sin(wt)$ we can approximate $v = \left| \frac{dz}{dt} \right|$, therefore there is a relation between linear and angular velocities $v = z_{max}w$. Furthermore, since usually $d_0 \ll z_{max}$ ($d_0 \sim 10\mu\text{ m}$, $z_{max} \in [\text{mm}, \text{cm}]$), one can conclude that Eq. (2.29) is in agreement with the one obtained in Ref. [52].

These results are all estimates, calculated from various assumptions: CS mode, either uniform approaching velocity or sinusoidal motion. In reality, the optimum resistance value is usually found experimentally from the search for the maximum power value, sweeping the available resistances. Typically, the optimum resistance is in the order of $M\Omega$ to $G\Omega$ [48]. Nonetheless, these estimations provide valuable information about the parameters that can be tuned in order to decrease (more commonly) or increase the value of the optimum resistance. One important strategy is increasing the dimensions of the layers, since the area will scale quadratically. Moreover, increasing the approximation velocity of the layers $\left(v = \left| \frac{dz}{dt} \right| \right)$, or the frequency ω , will also reduce the optimum resistance [47, 53].

There is an analytical solution for $\sigma_I(t)$, although the integration of $z(t)$ in time is always needed [49, 56], hence the result will always depend on the harvested vibration. For that reason, here the numerical approach will also be taken. From Eq. (2.10) with the electric potential in the form of Eq. (2.21), one obtains:

$$Z \frac{dQ(t)}{dt} = -\frac{Q(t)}{C[z(t)]} + V_{OC}[z(t)]. \quad (2.31)$$

This equation is equivalent to Eq. 2.19. Solving any of them for the induced charge $\sigma_I(t) = Q(t)/A$ allows the representation of current, voltage and power as functions of time.

2.3.3 Comparison between models

The two models were simulated, firstly for the parameters in Table 2.1, to compare the induced charge σ_I , the voltage/current response and establish the differences in the IVP curves.

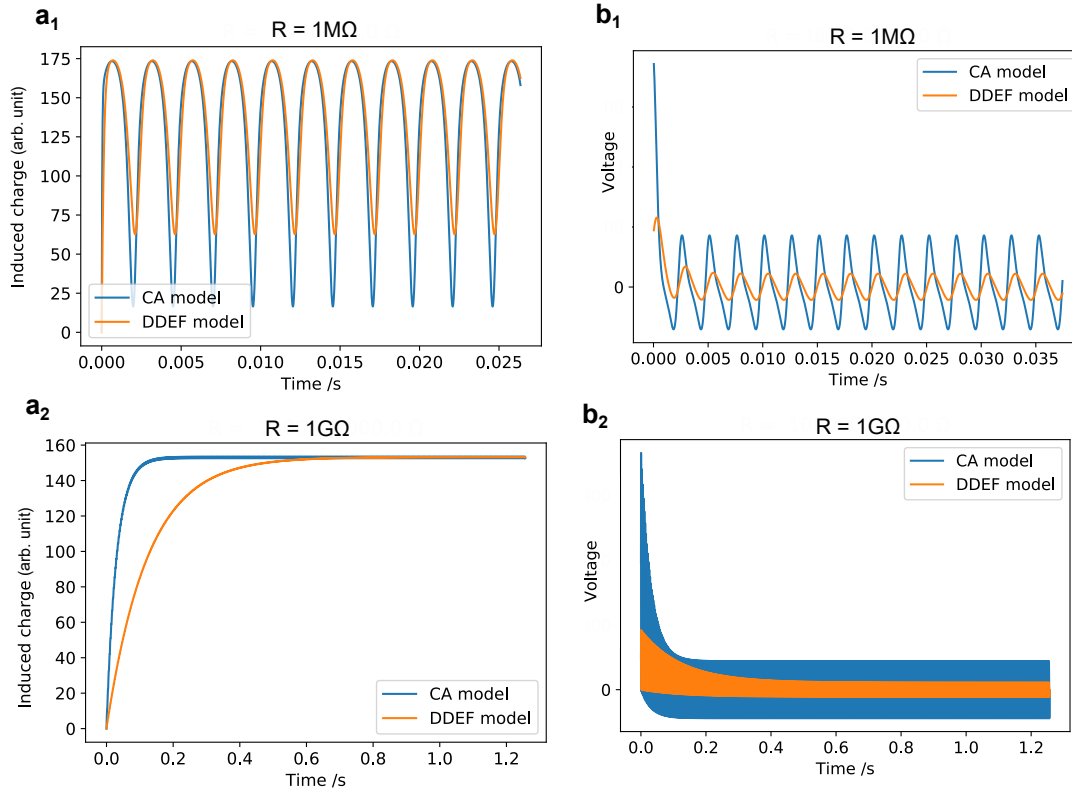


FIGURE 2.10: Results for the: a) induced charge; b) voltage (arbitrary units) for the CA and DDEF models, at intermediate (1) and high (2) resistance values.

The first observation is that while the shape of $\sigma_I(t)$ between models is the same, the CA model overestimates the value of σ_I , current and voltage, as shown in Figs. 2.10.a₁, b₁. Another difference concerns the transient regime. This regime occurs at the beginning of the solution $\sigma_I(t)$ and is characterized by a variation between the initial condition and the solution steady state. In fact, when there is a high impedance connecting the electrodes, the charges need more time to be induced (result of a very small current for high impedance) comparing to the case of connecting them with a small impedance, and this creates the slow transient regime visible on 2.10.a₂. After the transient, the solution is no longer distorted and stabilizes in a periodic function, therefore, the final time of the simulation must always be tuned in order to surpass it. Each model has a transient regime, longer for higher resistances (Figs. 2.10.a₂, b₂), and longer for the DDEF model than for the CA model. Note that for $1\text{G}\Omega$, the induced charge never decreases to near zero values

as it does for $1\text{ M}\Omega$ (see Figs. 2.10.a₁, a₂), as a result of the negligible current that flows between the electrodes for high impedances. In fact, it oscillates around a value near the maximum σ_I for $1\text{ M}\Omega$, with a such a small amplitude relative to that mean value, that one can say it stays constant throughout all contact separating cycles.

Regarding the resistance response, both models seem to agree on the prediction of the short circuit current (see Fig. 2.11.a). As the resistance increases, the shape of both current and voltage start to deform from the peak configuration in Fig. 2.11.a to a sinusoidal in Fig. 2.11.b (since the distance between layers $z(t)$ was a sinusoidal function). In fact, the open circuit voltage is sinusoidal not only for the CA model, but for the DDEF model as well. However, as the load increases the distinctions begin. The DDEF model predicts an earlier region II, since the current starts to decrease at a smaller resistance value than for the CA model. As a result, region II is displaced towards smaller resistances, as represented in Figs. 2.11.c,d. Additionally, for the DDEF model the open circuit voltage is reduced by a factor of 4, approximately (see Fig. 2.11.b). These two factors lead to an attenuated power curve with an optimum resistance shifted to a smaller value for the DDEF model (see Fig. 2.11.d), although this shift is smaller than one order of magnitude, from $124\text{ k}\Omega$ to $562\text{ k}\Omega$.

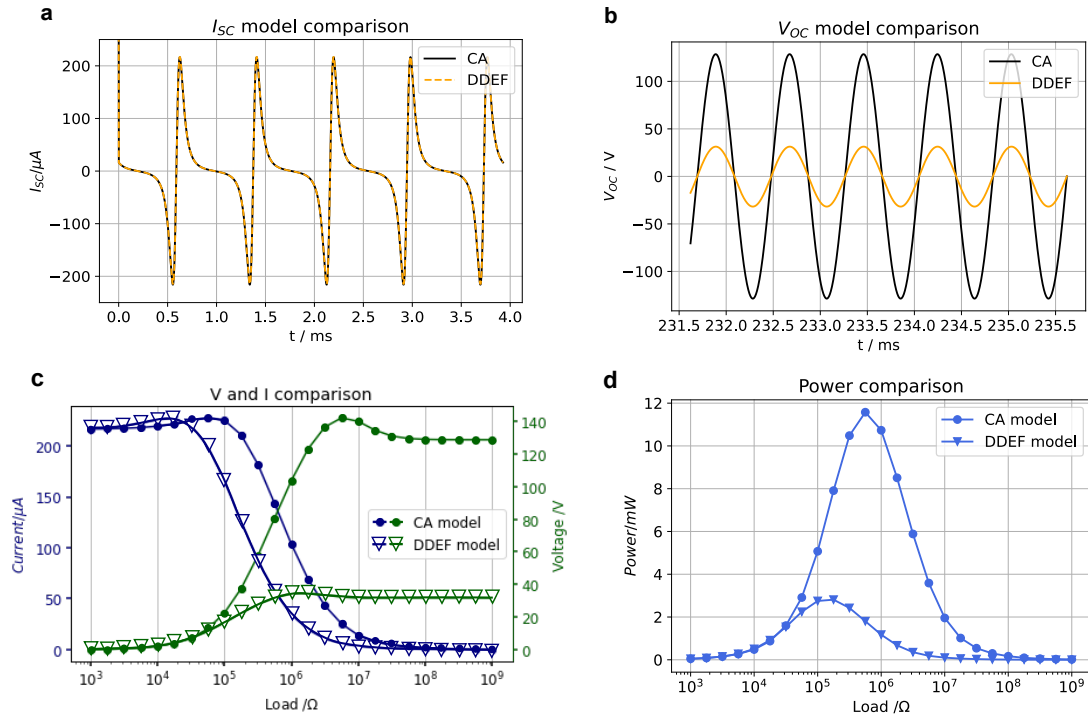


FIGURE 2.11: Comparison between CA and DDEF models for the first set of parameters of the: a) short circuit current; b) open circuit voltage; c) current and voltage; d) power.

In order to better understand the TENG that will be studied, the models were compared for a different set of parameter values, closer to the represented in table 2.2. The triboelectric layers Nylon and PTFE had their thickness reduced comparatively with the first set of parameters in table 2.1, and the maximum separation distance was slightly increased. Note that the period $T = \frac{2\pi A_z}{v}$ was also modified due to A_z , in order to maintain the same layers approximation velocity v - this can be seen comparing Figs. 2.11.a and 2.12.a. It should be noted that the objective of this second simulation was not to study the influence of any parameter in particular on the models predictions, but only to simulate more accurately the TENG that will be studied.

Parameter	Value	Parameter	Value	Parameter	Value
d_1	17 μm	d_2	50 μm	A_z	545 μm
Function $z(t)$	$(A_z + 5 \mu\text{m}) + A_z \sin\left(\frac{v_i}{A_z} t\right)$				

TABLE 2.2: Parameters that were changed from table 2.1 and their new values, used in the models comparison represented on Figure 2.12.

Regarding the second study, now short circuit current is overestimated by the CA model (see Fig. 2.12.a). Comparatively with the first set of parameters, the peak value of the short circuit current increased for the CA model, as predicted by the I_{SC} Eq. 2.20 and the new parameters on table 2.2, but decreased for the DDEF model (see also Fig. 2.12.c). On the other hand, the open circuit voltage was greatly reduced from the first set of parameters for the CA model, but barely unchanged for the DDEF model, causing V_{OC} to become closer in value between the two models (see Fig. 2.12.b). As for the maximum power, the values calculated by the two models also became closer, majorly due to the decrease of maximum power for the CA model. An important observation is that the optimum resistance is now the same for both models, with value of 124 k Ω , as it can be seen on Fig. 2.12.d. In summary, for the second set of parameters, the CA model agrees with the DDEF model on the optimum resistance, but keeps its tendency to overestimate all values of current, voltage and power.

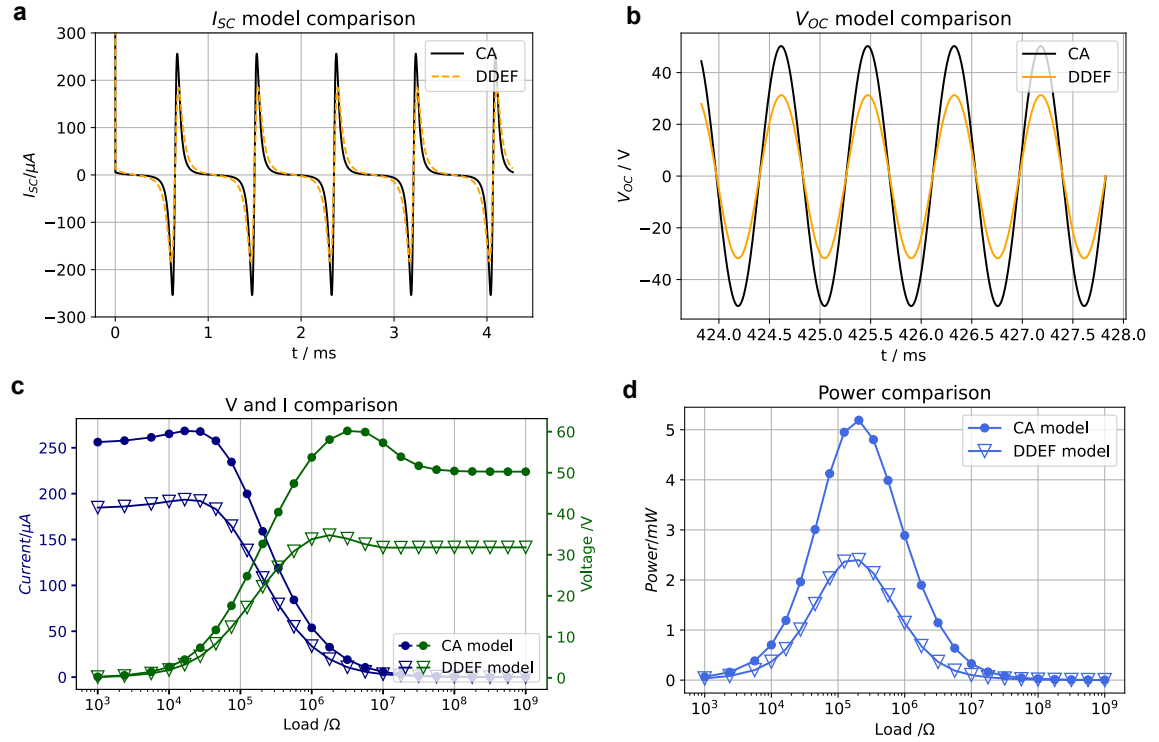


FIGURE 2.12: Comparison between CA and DDEF models for the second set of parameters of the: a) short circuit current; b) open circuit voltage; c) current and voltage; d) power.

2.4 Ocean waves energy harvesting

As referred at the beginning of this chapter, the ability of TENGs to continuously collect energy from low frequency oscillations, easy encapsulation and light weight, plus their versatility and simplicity of operation make them a suitable technology for ocean wave energy harvesting. On this section, the energy source of interest for this work, the ocean, will be detailed, followed by a review of some representative TENGs developed for ocean wave energy harvesting.

2.4.1 About ocean waves

The oceans cover almost two thirds of the Earth's surface and play a crucial role on driving local climates, integrating the carbon cycle, regulating the global temperature and hosting diverse and fundamental ecosystems for life on Earth. In their turn, they get directly influenced by the wind and the gravitational field of the Moon. The first one generates disturbances on the water surface and creates surface waves, either locally or over large distances [57]; on another hand, the Earth-Moon system creates a stretching force on these

large water masses, creating tidal waves with a characteristic period of roughly half a day that are not directly observable by eye. Other phenomena can be at the origin of waves, such as displacements of oceanic crust, earthquakes and storms. The potential and kinetic energy these waves possess represents an immense energy resource, estimated at 32 000 TWh/year [58], a value of the same magnitude of the 173 000 TWh consumed globally in 2019 [59]. Despite the feasibility of the consumption of this energy on land, it cannot be neglected by local, human built energy consumptive devices, and therefore, energy harvesting technologies.

A sea state is a complex set of waves at a particular place, and is characterized by several parameters, either in time, frequency, directionality or probability of occurrence [57]. These include their period, height and significant height H_s (average of the highest 1/3 of wave heights recorded in a fixed observation time). From the energy density spectrum of a oceanic state it is possible to identify the peak or dominant period T_p , correspondent to the highest energy density [57]. These two parameters, together with the mean direction θ_m obtained from a directional spectrum, are the three most used parameters in coastal engineering [57, 60]. Finally, a statistical approach is useful to describe and predict the waves behavior from data acquired over long periods of time, usually some years or decades [61–63].

The global distribution of the value of these and other parameters can be consulted on waves atlas, as represented in Figs 2.13 and 2.14 [64]. The presented data was recorded between 1970 and 2015 by Voluntary Observation Ships and analyzed in a UE funded cooperative initiative between universities and institutes in Moscow, Netherlands and USA. According to this study, the global significant wave height lies in the interval $H_s \in [1, 4]$ m and the dominant or peak period fulfills $T_p \in [3, 8]$ s. The reported accuracies are 0.5 m for heights and 1 s for periods.

Additionally, another source made a statistical study on both mean wave period T_m and H_s from the ERA40 dataset [62] of global meteorological variables within the years 1957-2002. The most frequent values for the mean period were $T_m \in [5, 9]$ s and the most of significant heights were in the interval $H_s \in [1, 6]$ m [65]. Based on the analysis of the ERA40 [62] and Topex/Poseidon[63] datasets in the years 1992-2001, another study showed most frequent $T_m \in [4, 8]$ s and $H_s \in [0, 4]$ m [66]. A similar evaluation for the portuguese coast was performed with one buoy data, located near Sines, detecting the range $H_s \in [1, 4]$ m as the one that contains the most occurrences [67]. All these values

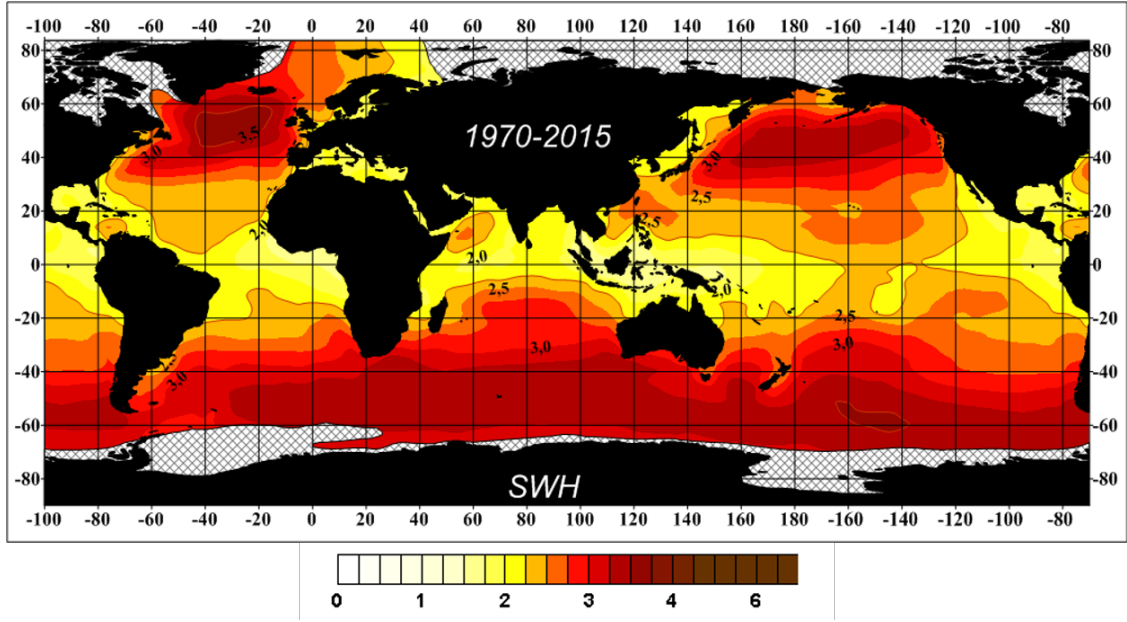


FIGURE 2.13: Global atlas of waves significant wave height H_s , data from an initiative between universities and institutes in Moscow, Netherlands and USA, recorded in 1970-2015 [64].

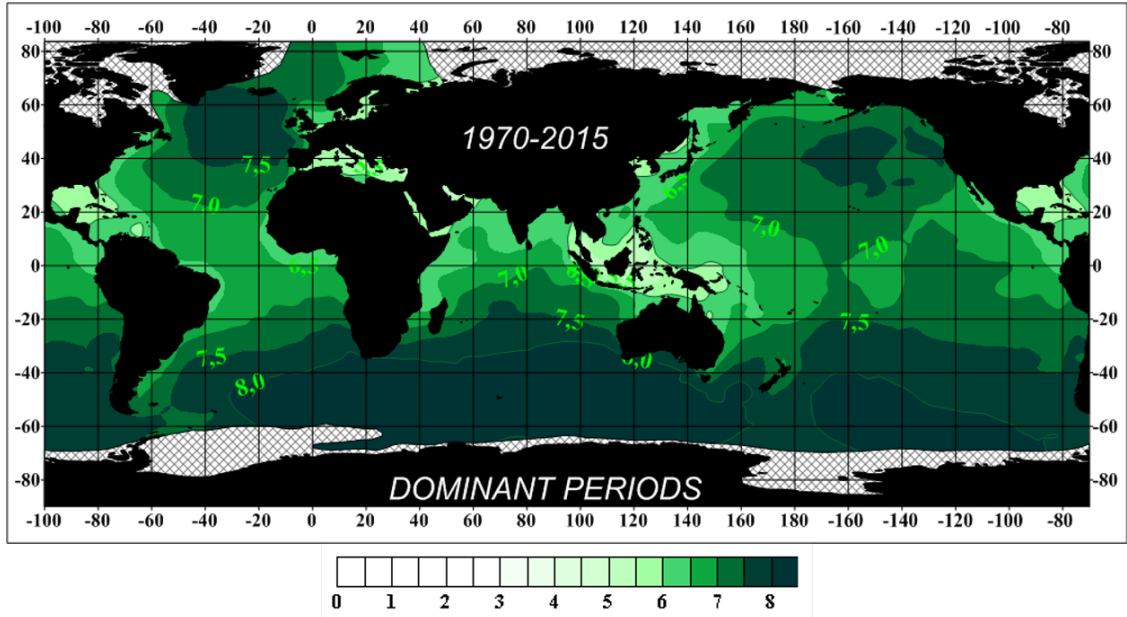


FIGURE 2.14: Global atlas of wave dominant periods T_p , data from an initiative between universities and institutes in Moscow, Netherlands and USA, recorded in 1970-2015 [64].

have an accuracy limited to several constraints, from the buoys acquisition to the analysis methods, introducing bias and errors that are presented in detail on the reviewed articles. Considering the reviewed values for period and specific height of waves, the maximization of the harvested energy, more than on materials choice for TENGs, depends on design to fit the most relevant waves at a particular site. In other words, TENGs structure must

allow them to make the most of the buoy motion induced by their deployment site waves.

Ocean buoys possess 3 rotational and 3 translational degrees of freedom, along each of the xyz axes. They are named roll, pitch and yaw for rotational movement, surge, sway and heave for displacement along each axis, respectively [68], as represented in Fig. 2.15.

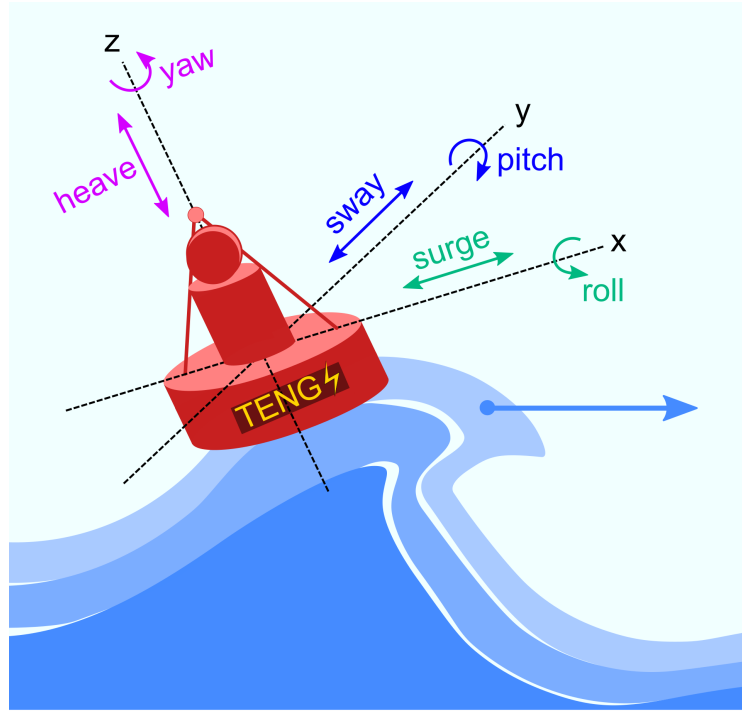


FIGURE 2.15: Rotational and translational degrees of freedom an ocean buoy is subjected to. The blue arrow is the phase velocity of the wave, with which the x-axis is aligned.

There are near 2700 offshore buoys [69] on continuous operation all over the Earth's oceans, playing a role in a variety of activities: weather forecasting, oceanography, maritime navigation, aquaculture, surveillance and others [68]. Some examples of ocean sensors and their power consumption are presented on Table 2.3. These electronic devices are usually powered by batteries, sometimes recharged by small solar panels (dependent on sunlight) or wind turbines (very expensive and dependent on wind) [68]. Moreover, in remote places, the replacement of batteries and maintenance of the whole system add further costs.

Therefore, new scalable, low cost and truly continuous sources are necessary, even better if they are self-powered, autonomous, systems. This technology gap can be filled by TENGs with a power management system able to recharge the batteries, enclosed in buoys along with the sensors or small devices they aim to power [68].

Sensor type (model)	Power (mW)	Ref
Pressure, temperature and humidity (PHT MS8607-02BA01)	$[1 - 72] \times 10^{-3}$	[70]
Partial CO_2	2.9	[71]
Analog Pressure (11-1107-DS)	5-50	[72]
Wind speed (ISAW WindFlowWF4)	13-63	[73]
Wave height (3505)	25-49	[74]
Turbidity (4112)	24.5-70	[75]

TABLE 2.3: Examples of ocean sensors and their power consumption.

2.4.2 TENGs for ocean waves energy harvesting

A multitude of ocean waves harvesting TENGs has been developed, which can be divided in three categories according to the nature of their contacting area: single point (for instance, a sphere promoting the contact of the layers), multi point (several spheres over the layers or stacked units of one sphere) or single area (contact on a surface). To make the most of all the degrees of freedom, the spherical shape occurs frequently [4], as the encapsulating structure of the TENG and/or in rolling spheres that promote contact between other layers [76, 77] or act directly as a triboelectric material [78–81].

For the single point typology, one stresses the work of Z.L. Wang *et al.*, that in 2015 developed the first spherically enclosed TENG for ocean wave energy harvesting, the RF-TENG (rolling freestanding; see Fig. 2.16.a) [54]. The first version of the RF-TENG was composed of a PTFE sphere pressing directly the Al electrodes along the inner surface of the encapsulating sphere (see Fig. 2.16.a), and the improved version consisted of a Nylon sphere contacting Kapton over the Al film, inside the same spherical structure, as represented in Fig. 2.16.b. After optimizing the diameter of the inner sphere to 4 cm (while the encapsulating sphere was kept at a 6 cm diameter), under a 1.43 Hz wave frequency the Nylon version of the RF-TENG showed short-circuit current of $1.2 \mu A$ and 12000V at

10 G Ω , that however did not correspond yet to the open circuit voltage, since the optimum resistance was not achieved (see Fig. 2.16.e), due to the small internal capacitance. This resulted in a maximum power of 10 mW for one RF-TENG unit, and knowing the size of the encapsulating sphere, a power density of 88.46 W/m³ is calculated, however remembering that this value corresponds to a very high load of 10 G Ω .

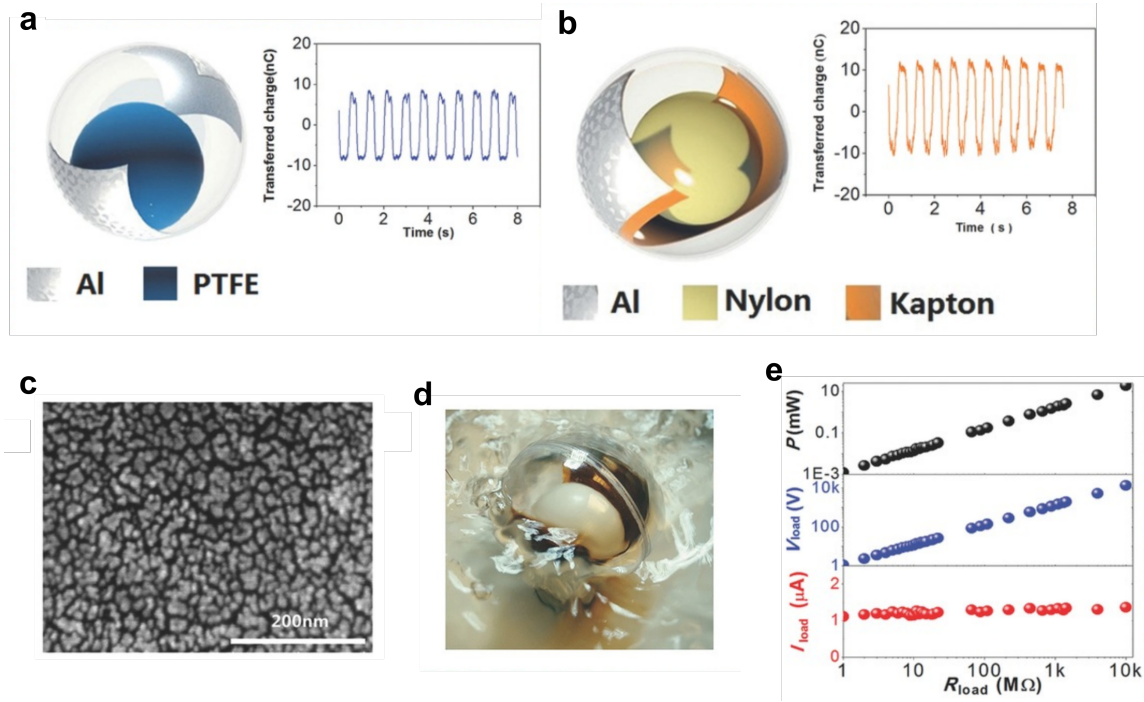


FIGURE 2.16: The RF-TENG developed by Z.L. Wang *et al.* (2015). a) Schematic of the first version with PTFE/Al as the triboelectric pair; b) The improved version with the Nylon/Kapton pair; c) SEM image of nanorod structure on the Kapton surface; d) Electrical outputs (current, voltage and power) of the Nylon/Kapton device for several load resistances. Adapted from [54].

The multi contact category concerns TENGs where contact occurs at multiple points, occurring at different sites, simultaneously. We stress three representative devices under this category. First, Xu *et al.* (2019) created the T-TENG (tower-like) [80] represented in Fig. 2.17.a, constituted by PTFE spheres rolling over a Nylon film inside a spherical arc structure. Due to its small height, researches were able to stack several units vertically, achieving the tower shape. With 10 units and after optimizing the spheres diameter and number, under a linear motor excitation of frequency 1.6 Hz and 150 mm amplitude (see Fig. 2.17.b), a short circuit current of $\approx 8 \mu$ A and an open circuit voltage of ≈ 6000 V were obtained, achieving 10.6 W/m³ at the ≈ 110 M Ω optimum resistance (see Fig. 2.17.c). Another interesting device was developed by Yang *et al.* (2019) [82] where, inside an encapsulating sphere, were stacked several floors of spheres of fluorinated ethylene

propylene (FEP) rolling in between two Cu electrodes, always in contact with them, as represented in Fig. 2.17.d. For a single unit, at the optimum resistance of $1\text{ G}\Omega$ an average power density of 8.69 W/m^3 under 1.67 Hz , 100 mm linear agitation was obtained on a dry test (see Fig. 2.17.e). After the stacking inside each ball, the researchers developed a magnetic connecting system between the units, so that they would self-assemble on various configurations as represented in Fig. 2.17.f. For 18 units connected in a line, subjected to 1.45 Hz waves, the device performed the best at $50\text{ M}\Omega$, with 2.05 W/m^3 power density, showing the importance of conducting tests on a water environment. Recently, Wang *et al.* (2021) published a tower-like structure where each stacked element was a sandwich of PTFE balls between Al electrodes, the S-TENG (sandwich-like TENG) [14]. This configuration (with 10 layers) allowed better utilization of space as it is evidenced by the power density of 34.65 W/m^3 (corresponding to $12.28\text{ }\mu\text{A}$ of short circuit current), under 2 Hz and 130 mm amplitude linear motion. The researchers then connected 7 units (70 layers in total) in a hexagonal close packed configuration, as represented in Fig. 2.17.g, having concluded that the maximum values of charge, current and power increased linearly with the number of the parallel connected units, achieving a peak power of $\approx 80\text{ mW}$, comparatively to 10 mW for a single unit (see Figs. 2.17.h, i). For all these devices, the optimum resistance decreased for the network of TENGs, since they were connected in parallel. Additionally, considering that the spheres of different units can be slightly out of phase, in the last two articles, each TENG unit was rectified before being connected to the others.

Making advantage of a larger area of contact between triboelectric layers, on the single area category we will also discuss three devices. The first, by Cheng *et al.* (2019) [78], has a structure similar to the point contact RF-TENG, with the difference that the inner sphere is soft and made from silicone rubber. This way, the sphere deforms to contact the electrodes of copper in a large area (see Fig. 2.18.a), improving the transferred charge between electrodes 10 times comparatively with a regular rigid PTFE sphere tested on the same device. For a 50 mm and 2 Hz linear oscillation amplitude, the SS-TENG (soft-contact spherical) reaches 280 V of open circuit voltage, $5\text{ }\mu\text{A}$ of short circuit current and 1.8 mW of power at $200\text{ M}\Omega$, as represented in Figs. 2.18.b,c. For a higher frequency of 5 Hz , the authors reported a maximum power of 10 mW . From the diameter of the encapsulating sphere (7 cm), it is possible to calculate power densities of 10.02 W/m^3 and 55.68 W/m^3 for 2 Hz and 5 Hz , respectively. Liang *et al.* (2020) [83] created a charge excitation circuit (CEC) to improve their device performance, a spring-assisted TENG based on the contact of FEP

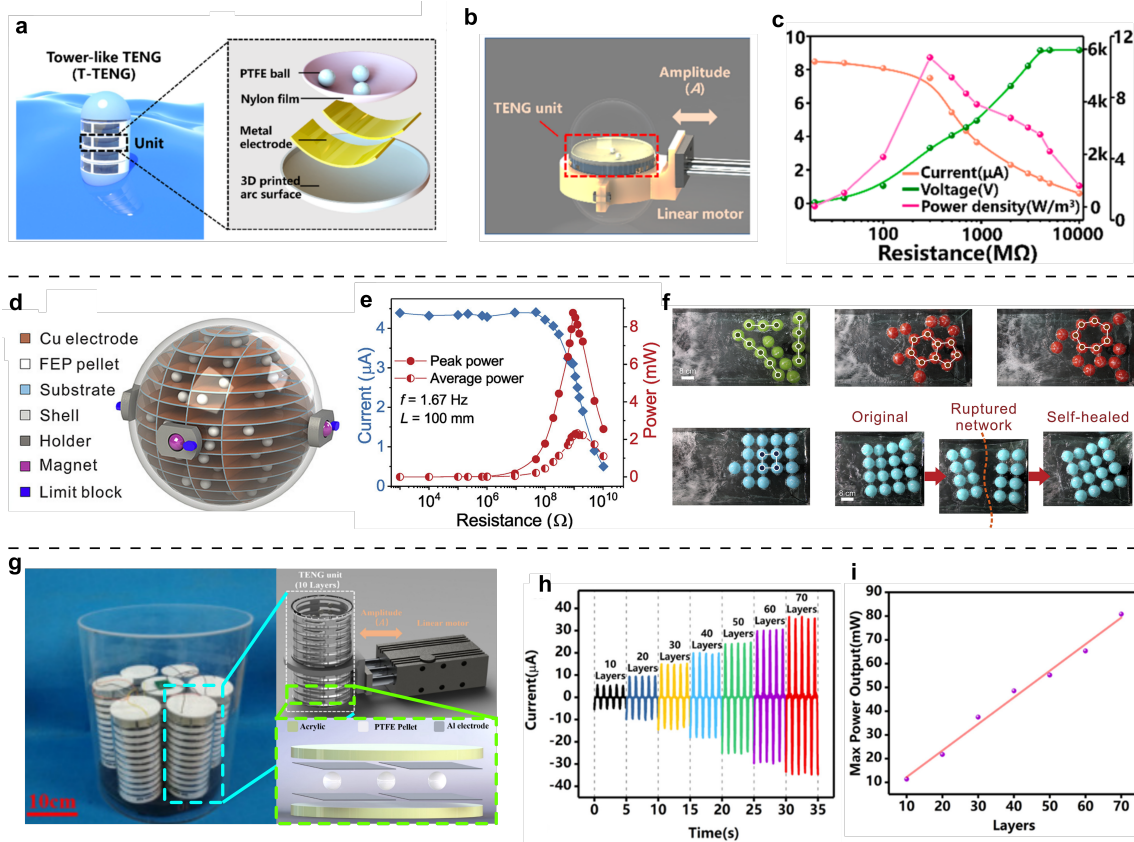


FIGURE 2.17: Multi contact TENGs for ocean wave energy harvesting: a-c) T-TENG [80]; d-f) Magnetically attached TENG [82]; g-i) S-TENG [14]. a) Schematic of the device structure; b) Linear motor test setup for one unit; c) Electrical output for the 10 stacked units for a linear oscillation of 1.6Hz and 150 mm; d) Device structure; e) Electrical output for one spherical unit under a linear test of 1.67Hz, 100 mm; f) Different self-assembled network configurations according for 2 (green), 3 (red) or 4 (blue) magnetic joints; g) Composition of each sandwich layer, a unit composed of 10 layers, and a hexagon arrangement with a total of 70 layers; h-i) Short circuit current and maximum power with the number of layers.

and Al planar layers, as represented in Fig. 2.18.d. For waves of 100 mm amplitude and only 0.6 Hz, they achieved 25.1 mA of maximum current and 25.8 mW output power at the remarkably low resistance of 300 Ω (since the CEC had a higher equivalent capacitance, reducing the value of the matched resistance) with a corresponding power density of 49.3 W/m³. Although the integration of seven TENG units was reported to increase the density of output current peaks, it did not affect the maximum current and power (changed to 24.5 mA and 24.6 mW, respectively, as shown in Fig. 2.18.e,f) due to the asynchronous movement of the TENG units (note that rectifying bridges were not used). This year, another design based on contacting several planar surfaces was published by Zhang *et al.*, with promising results [84]. The BM-TENG (bifilar-pendulum multilayered) was composed of several folded layers of Cu and nanostructured FEP, resembling a fireplace

bellow, pressed and released simultaneously by a pendular structure (see Fig. 2.18.h). With this device, a power density of 200 W/m^3 at $5 \text{ M}\Omega$ was obtained, under 20° rotation in a seesaw. Even for a small angle of 5° , a short circuit current of $120 \mu\text{A}$ and open circuit voltage of 400 V were achieved. When subjected to realistic conditions, on wave heights from 100 to 200 mm and frequencies in the range 0.2 Hz to 1 Hz , a power density of 34.7 W/m^3 at a loading resistance of $2 \text{ M}\Omega$ was reported (represented in Fig. 2.18.i). For the same conditions, the reported short circuit current and open circuit voltage for each side of the BM-TENG were $60 \mu\text{A}$ and 400 V , respectively. The authors also verified that increasing the number of layers and wave heights improved the output of the BM-TENG.

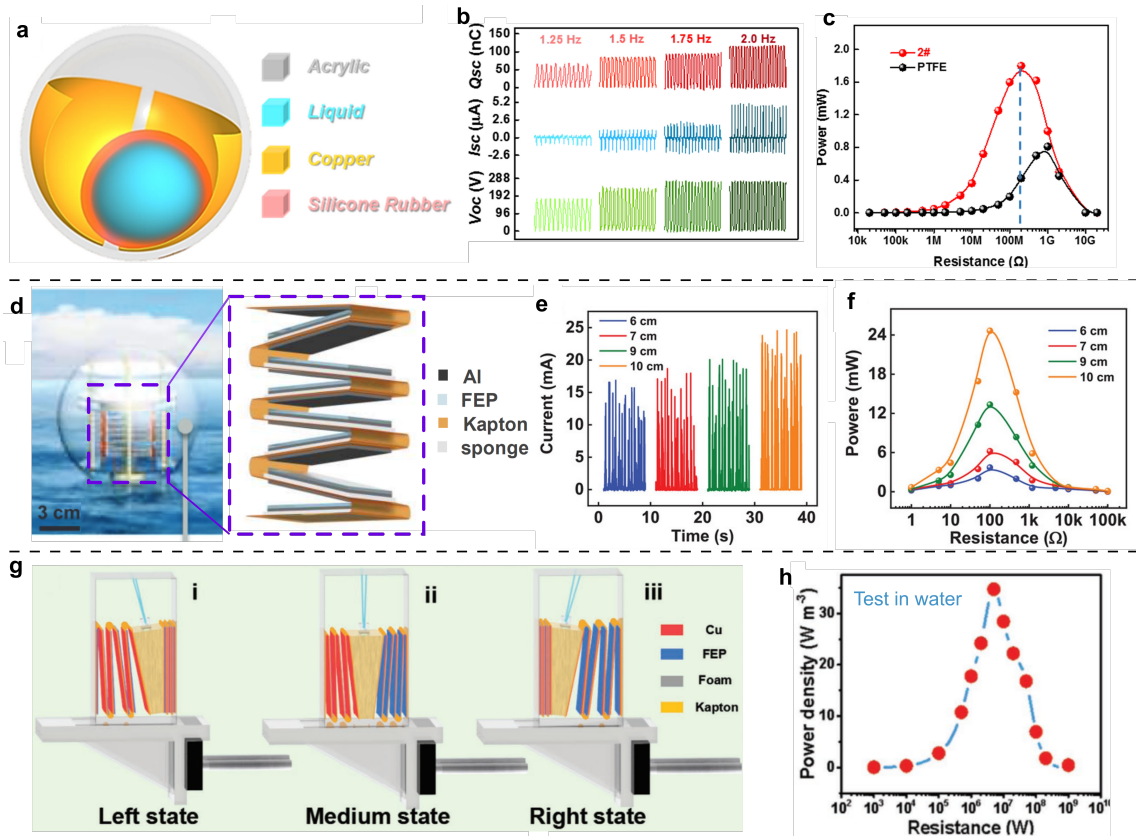


FIGURE 2.18: Examples of single area TENGs for ocean wave energy harvesting: a-c) SS-TENG [78]; d-f) Spring-assisted TENG with a CEC [83]; g,h) BM-TENG [84]. a) SS-TENG structure; b) Charge, current and voltage for different frequencies and 50 mm of linear oscillation; c) Power of the soft TENG (red) and a rigid version (black) for 2 Hz and 50 mm ; d) Device structure schematic; e) Current and e) Power of 7 units for different wave heights and 0.6 Hz frequency; g) BM-TENG structure, showing the pendulum establishing the contact of the TENGs on the right and separation on the left simultaneously (i) and vice-versa (iii); h) Power density for $0.2\text{-}1 \text{ Hz}$ and $100\text{-}200 \text{ mm}$ waves.

For this brief review, the electrical characteristics on water tanks were presented whenever provided by the respective article, in addition to the standard linear, unidirectional

test, maintained here for fair comparison between devices. However, many studies only presented the charging of one or more capacitors when subjected to water waves. Hence, in Table 2.4 a summary of the characteristics and performance of the devices is presented, distinguishing as well the type of test (dry or wave basin).

Typology	Test, f/Hz , A/mm	$I_{SC}/\mu A$	V_{OC}/V	P_d / Wm^{-3}	Year & Ref
Single contact	waves, 1.43, NA	1.2	NA	88.46 ^a	2015 [54]
	dry, 1.6, 150	8	6000	10.6	2019 [80]
Multi contact	waves, 1.45, NA	NA	NA	2.05	2019 [82]
	dry, 2, 130	12.28	NA	34.65	2021 [14]
	dry, 2, 50	5	280	10.02 ^a	2019 [78]
Single area	waves, 0.6, 100	25.1	NA	49.3	2020 [83]
	waves, 0.2 - 1, 100-200	60 ^b	400 ^b	34.7	2021 [84]

^a Calculated considering the TENG encapsulating sphere, based on the provided diameter.

^b For each side (left/right) of the BM-TENG.

TABLE 2.4: Summary of the characteristics of recent TENGs for ocean wave energy harvesting. A stands for amplitude for dry tests and for wave height if the test was done on a wave basin. P_d is the volumetric power density.

2.5 Opportunities for research and motivation

Despite the current development of power dense TENGs, some challenges exist concerning the upscaling and long time applicability of this technology. First of all, only few studies exist on the degradation of TENGs [4, 85] and, depending on the each device design and contacting mode, this can be a limiting factor for the viability of the device [13]. Moreover, since they often have polymers on their composition, there are concerns on the fragmentation of such materials and their replacement for biodegradable options [85]. Another field open for research is the networking of TENGs. Different connection typologies were studied in a theoretical model, having described how cable resistance and output phase asynchrony between units can affect the network output power [86]. However, the field lacks a comprehensive study of the networking problem, and experimental investigation to corroborate this and other models to be developed [13, 86]. Also, the

performance of TENGs at ocean-like conditions and specifically inside buoys, in terms of relative humidity and temperature, needs to be studied. Power management is yet another ongoing topic with many strategies in development, from rectification, electromagnetic transformation, capacitive transformation (such as the CEC described earlier), and DC conversion, that have successfully reduced the matching impedance of TENGs and improved the transferred power [87]. Finally, there is a lack of systematic studies [4] on the performance of TENGs in different conditions of buoy period and amplitude of yaw, pitch or roll rotation to guide their design.

Although the main device studied will be detailed later, it is important to contextualize it on the reviewed literature. The unidirectional lateral TENG (UL-TENG, developed by Rodrigues *et al.* [4]), belongs in the single area category of the reviewed TENGs, while still making use of the rolling spheres characteristics of the single contact typology. In fact, it was developed as a prospective better version of single contact TENGs, the anisotropic circular-based (AC-TENG) and a unidirectional flat-based (UF-TENG) (see Fig. 2.19.a-c).

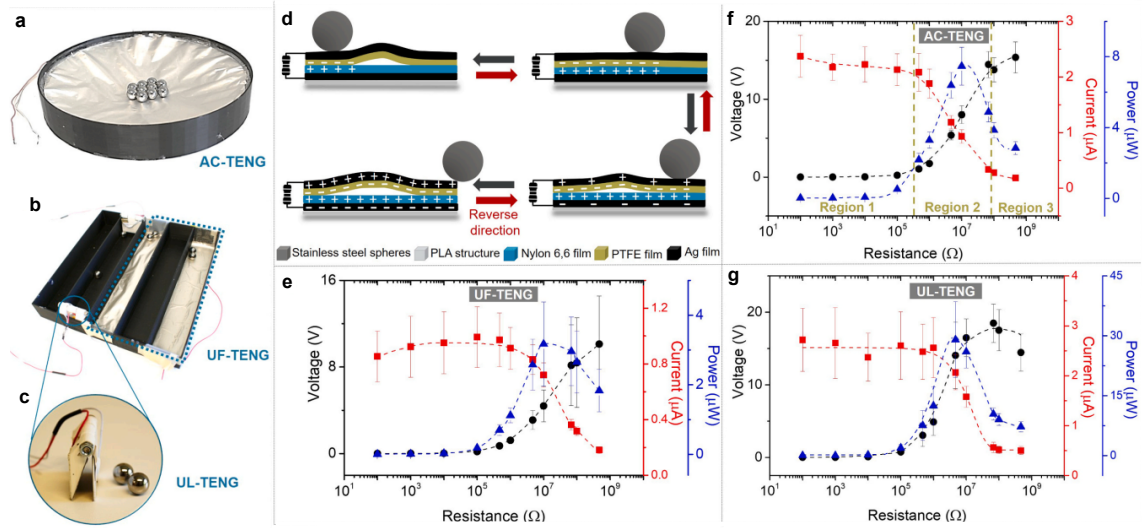


FIGURE 2.19: The TENGs that led to the development of the UL-TENG (c) and their typical output. a) anisotropic circular-based (AC-TENG); b) unidirectional flat-based (UF-TENG); c) unidirectional lateral TENG (UL-TENG); d) Working mechanism of the AC-TENG and and AF-TENG; e) IVP curve of the UF-TENG; f) IVP curve of the AC-TENG; g) IVP curve of the UL-TENG. Adapted from [4].

The AC-TENG and the AF-TENG are composed of rolling spheres over layers of Ag/Nylon on top of PTFE/Ag layers. As depicted in Fig. 2.19.d, when the spheres roll in a given direction, they press a portion of the Nylon and PTFE layers together, to immediately after press another portion ahead on their trajectory, leaving the portion of the

layers left behind free to separate. With time, the layers glue together due to the electrostatic attraction, reducing the maximum separating distance between layers. On the other hand, the UL-TENG did not depend on this mechanism of separation of the triboelectric layers, dependent of their tension and elasticity, since the triboelectric layers are fixed on rigid parts, increasing the contact area comparatively to the AC-TENG and AF-TENG. Therefore, the UL-TENG outperformed them both (see Fig. 2.19.f-g), while keeping the rolling spheres as the contacting mechanism.

Therefore, the main challenge tackled by this dissertation is investigating how the buoy dynamics affect the power output of a given TENG in order to optimize its performance. Can the velocity of the rolling spheres be the linking parameter between the dynamics and the output of the UL-TENG? Furthermore, other routes to the optimization of TENGs were taken: the coupling of two generators and the fabrication of PTFE thin films for more control of this triboelectric layer properties. During the next chapters, it will become clear how that was performed and what the optimization of a particular device can look like.

Chapter 3

Methods of fabrication, characterization and analysis

We shall now describe the tools that were used and/or developed for the following work. First, we will present the acquisition and motion system developed to conduct the measurements of current and voltage, under different conditions, of our device. Second, the fabrication and characterization methods carried out to perform a study on the deposition of PTFE from aqueous solutions for future TENG applications will be detailed.

3.1 Automatic Acquisition and Motion System

Measuring a TENG performance requires the acquisition of current and voltage under a reproducible motion. Before the execution of this work, these two tasks were executed and controlled separately, but since the number of tests was extensive, the need for automation was felt. A good number of tasks was already developed by other colleagues: programming the acquisition, selecting the resistors to use for each test and executing the motion for specific parameters, the first two interfaced to the user by the software Labview, and the last one by an Arduino Uno microcontroller (let it be Arduino Uno 1). Therefore, to run our tests smoothly, we designed a printed circuit board (PCB) (see Appendix A for the board schematic) for commuting the voltage and current acquisitions without needing to manually change the connecting wires (that also allows the connection of more than one TENG) and combined all the parts in one Labview program, to minimize the complexity of setting up a specific measurement and the required time for a set of measurements.

3.1.1 Acquisition of current and voltage

To perform each acquisition we used the PCB Commutator controlled by Arduino Uno 1, a Keithley 6514 Electrometer, and a “Box of resistances”, a PCB with 11 different resistances and relays controlled by a second Arduino Uno (let it be Arduino Uno 2; schematic on Appendix A). The Commutator will close or open internal switches that link the Electrometer to both the TENG and load, connecting it either in series (for current measurement) or in parallel (for voltage measurement). Following Fig. 3.1, when B and C are closed, A is open, and the commutator is on the parallel state: both terminals of the Electrometer are connected to the terminals of the TENG and the load. When A is closed, B and C are opened, constituting the series state. On this state, the circuit is a closed loop, so that all current flows through the sensing Electrometer: for instance, from the red terminal to the load, then to the TENG and back to the Electrometer through the closed path A. Note that the Electrometer is either reading voltage or current, therefore they are acquired sequentially.

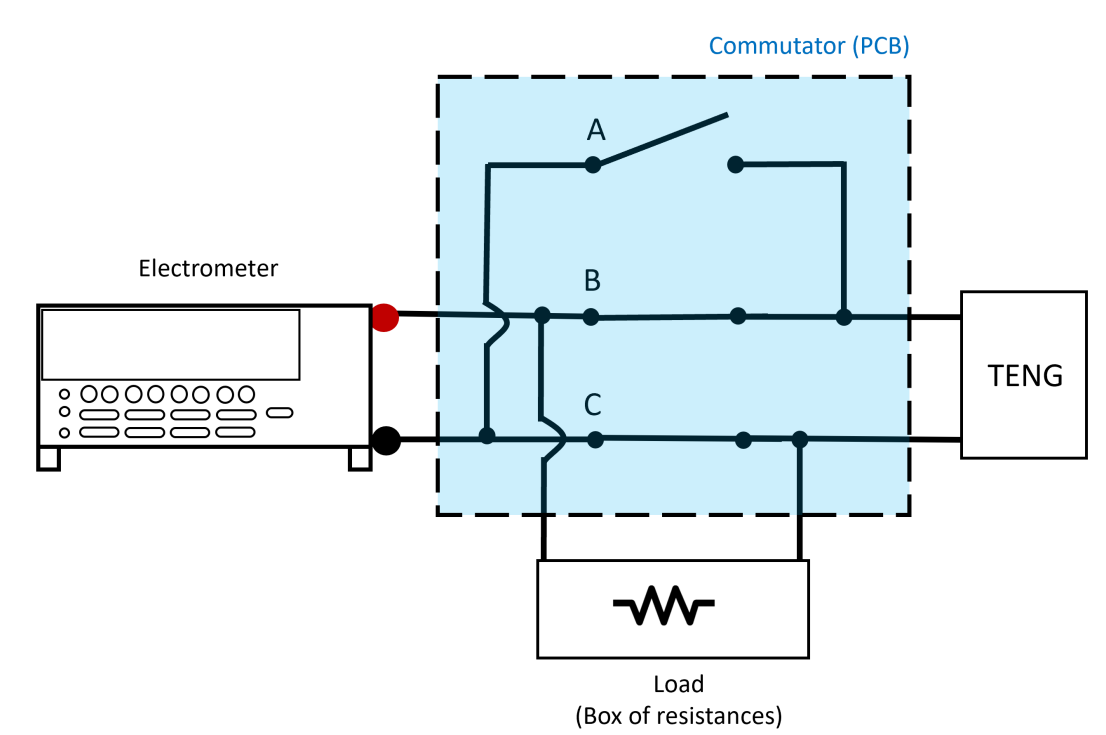


FIGURE 3.1: Schematic of the acquisition of voltage and current setup.

3.1.2 Rotative frame system

In its turn, the motion system utilized consists in a 1-axis rotating frame where the TENGs are mounted, tilted by a servo motor controlled by Arduino Uno 1. This motion system attempts to replicate the pitch rotation represented in Fig. 3.2, receiving as parameters the period of the motion T , in milliseconds, and the pitch A° , that is, the maximum angular amplitude from the zero (flat, parallel to the ground) position to each side.

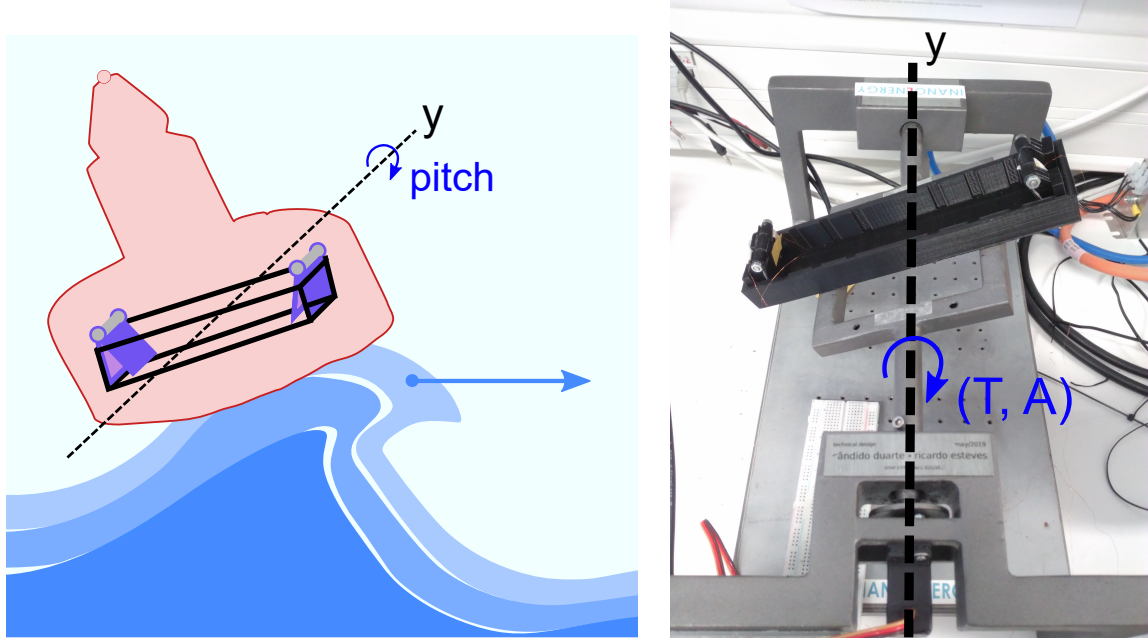


FIGURE 3.2: The pitch movement of a buoy when subjected to a travelling ocean wave, on the left; on the right, the equivalent motion on our rotative frame, parametrized by the period T and pitch A .

3.1.3 Integration of motion and acquisition

In order to understand the working of this integrated system, represented in Fig. 3.3, we shall follow the setting up of a test. There are three types of tests one can be interested in: current and/or voltage for one resistance only, the resistance response, or the performance for different wave conditions, at the optimum resistance. After opening the Labview program, the user can choose to measure one of three possible TENGs connected to the PCB commutator, or all of them sequentially; current, voltage or both sequentially. Then, she must choose the voltage and current ranges from the options the Keithley 6514 Electrometer has available. Then, she will choose which type of test wishes to conduct: in resistance or in period and amplitude. If the first one is chosen, she must specify if a

sweep of all available resistances is desired or only a measurement of a single resistance, and indicate the index of that resistance as in the table shown in the same Labview window. If the second option is chosen, she must specify at which resistance wants the study to be conducted on, and how many tests need to be conducted, equal to the number of periods times the number of amplitudes. Finally, she should specify the time duration of each measurement: either if it a single resistance measurement, each of the resistances of a sweep, or each of the pairs (T, A) .

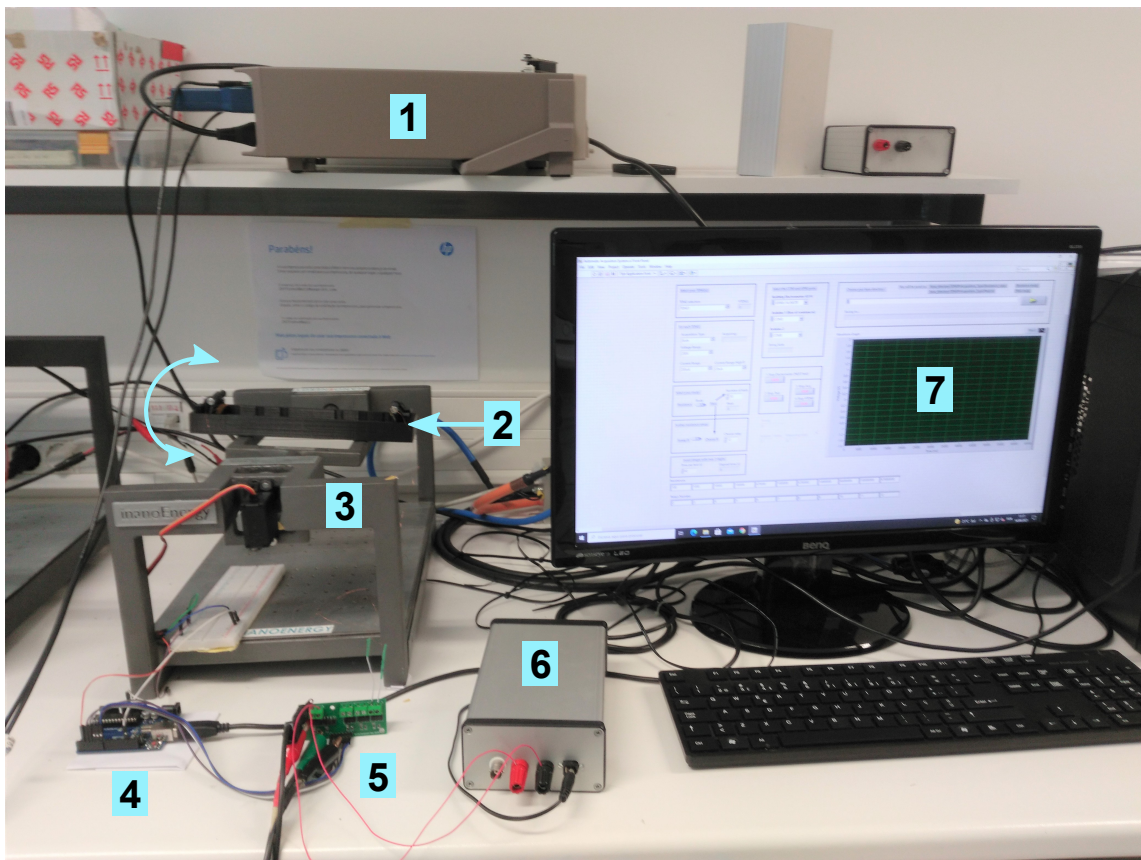


FIGURE 3.3: The motion and acquisition system: (1) Keithley 6514 Electrometer; (2) Device under test; (3) Rotative 1 axis frame; (4) Arduino Uno 1; (5) PCB commutator; (6) Box of resistances (Arduino 2); (7) Labview user interface.

These commands are sent to Arduino Uno 1 via a string, so that it knows if it needs to switch the PCB commutator to a different TENG or between voltage and current, and how many cycles of rotation it must execute for a specified test, or until one of those events.

This automation does not mean no intervention is needed at the Arduino Uno 1 level. The values of periods and amplitudes to be tested are inserted directly on the Arduino code. Likewise, if one is doing a resistance study, it also needs to choose a period and an amplitude for the rotating frame to move. This must be done at the Arduino Uno 1

level because otherwise, a string of variable length would have to be sent from Labview to Arduino Uno 1, making it impossible for Arduino Uno 1 to know how many values it would receive, that is, how much memory it needed to allocate beforehand to store the incoming data. In other words, creating variable length arrays of data is strongly inadvisable in C. Consequently, no simpler approach was found to automatically change from one value to an unknown quantity of values of periods and amplitudes besides inserting those values directly and commenting (or uncommenting) some well signaled lines of code inside the function that executes the servo motion. The operation, inputs and outputs of each component are described in detail on the manual of the system (included in Appendix B), as well as a quick start guide, written to accompany the user.

3.2 Measurement setup for PTFE samples

Testing the triboelectric response of samples when incorporated on a TENG requires a more predictable and controllable motion. Therefore, we used a linear pneumatic motor to contact and separate the triboelectric layers of interest. One side of the TENG (one triboelectric layer and electrode) is fixed on the moving end of the linear motor. The other side (other triboelectric layer and electrode) is fixed at a metallic plate firmly attached on a table, facing the mobile plate at a defined distance (see Fig. 3.4).

Since the linear motor depends on compressed air, perturbations on the measurements (excessive vibrations, rapidly varying pressure) can occur during the air compression. Since this occurs periodically, the longest measurement time without interferences implies starting the acquisition right after the air is compressed, and stopping it just before the compression starts. However, this means that the automation described on section 3.1, of measuring current and voltage for all resistances sequentially, is not possible. Therefore, the connections between series and parallel were switched by hand, and the resistances measured individually, although the same Labview program was used, provided that all inputs/outputs (Arduino 1 and 2, Electrometer) were connected to the PC. In summary, the acquisition for these samples is made with the same instruments as in section 3.1, but needs a much more thorough attention and input from the user.

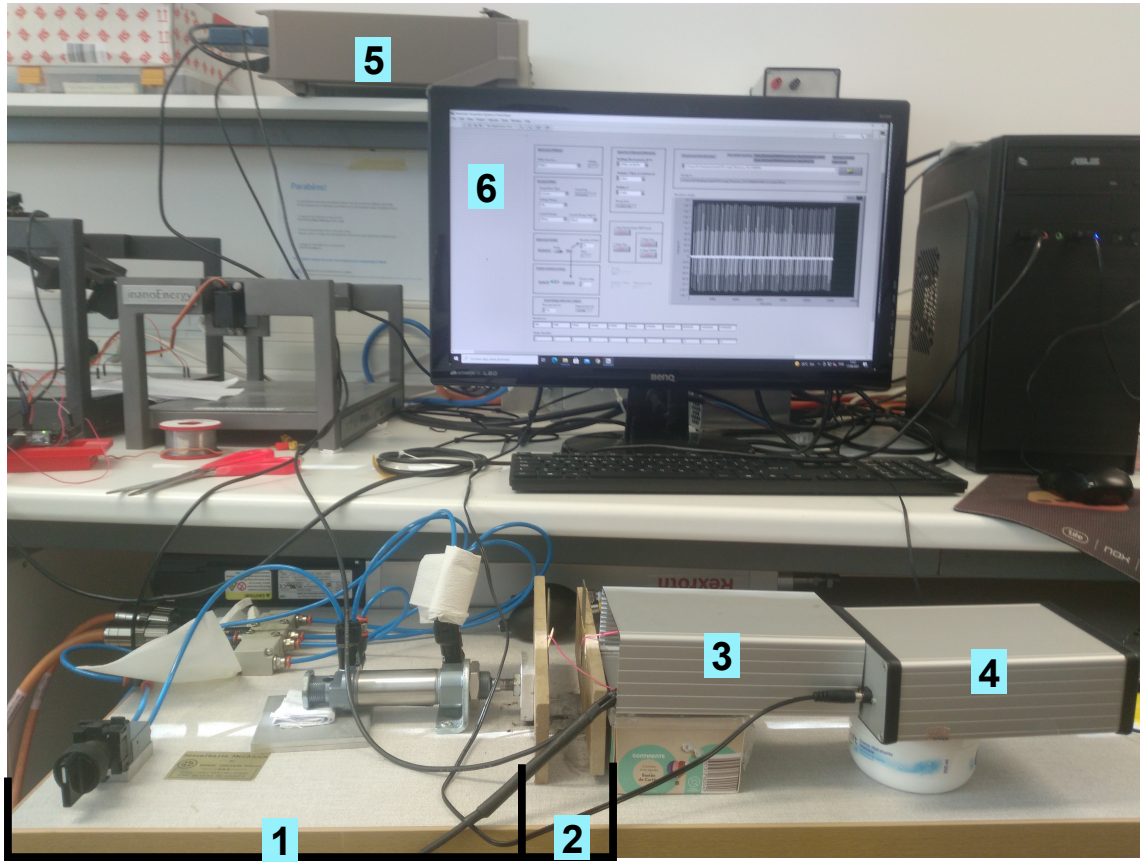


FIGURE 3.4: Experimental setup for the measurement of TENGs with PTFE thin film samples. (1) Linear pneumatic motor; (2) Mobile (left) and fixed (right) plates where the two side of the TENG are mounted; (3) Faraday cage protecting the TENG wiring; (4) Bof of resistances (Arduino 2); (5) Keithley 6514 Electrometer; (6) Labview interface.

3.3 Data analysis software

During the measurements of current and voltage in time, for several resistances or several pairs of period and amplitude, a huge amount of data was saved by Labview. This data was analyzed with a Python routine already developed, although modifications were done mostly in terms of graphic display and automation of folder search.

The used Python routine needs three parameters: period of motion, number of peaks per period and a variable β . First, it identifies the specified number of maximum and minimum peaks per period on a given file. For instance, if the device produces two peaks per period, it will divide the file on half periods and search for one maximum and one minimum value in each half period. Then, it calculates the mean value of the positive (let it be $\overline{X_p}$) and negative ($\overline{X_n}$) peaks, separately. However, a great standard deviation σ_p, σ_n can exist at this step, since very small peaks can still be detected in some half periods, that do not correspond to the real output of the device. For example, if the Electrometer

fails the acquisition of one positive and/or negative peak in a half period, the routine will choose noise peaks on that half period interval. To avoid this phenomena, only the peaks above the threshold $\overline{X}_p + \beta\sigma_p$ for the positive peaks and under the threshold $\overline{X}_n - \beta\sigma_n$ for the negative peaks (see Fig. 3.5) are preserved for the final step. For the final value of voltage/current of each test, one can then choose between the absolute maximum positive peak, the absolute maximum negative peak, the mean of those two absolute maximums, the mean of the positive peaks above the positive threshold, the mean of the negative peaks under the negative threshold, or finally the mean value of all the preserved positive and negative peaks. The latter was chosen for all measurements in this work, and saved as the final result. The electrical power correspondent to each test is calculated by this routine as the product of current and voltage, always from the mean value of all the preserved positive and negative peaks of current and voltage.

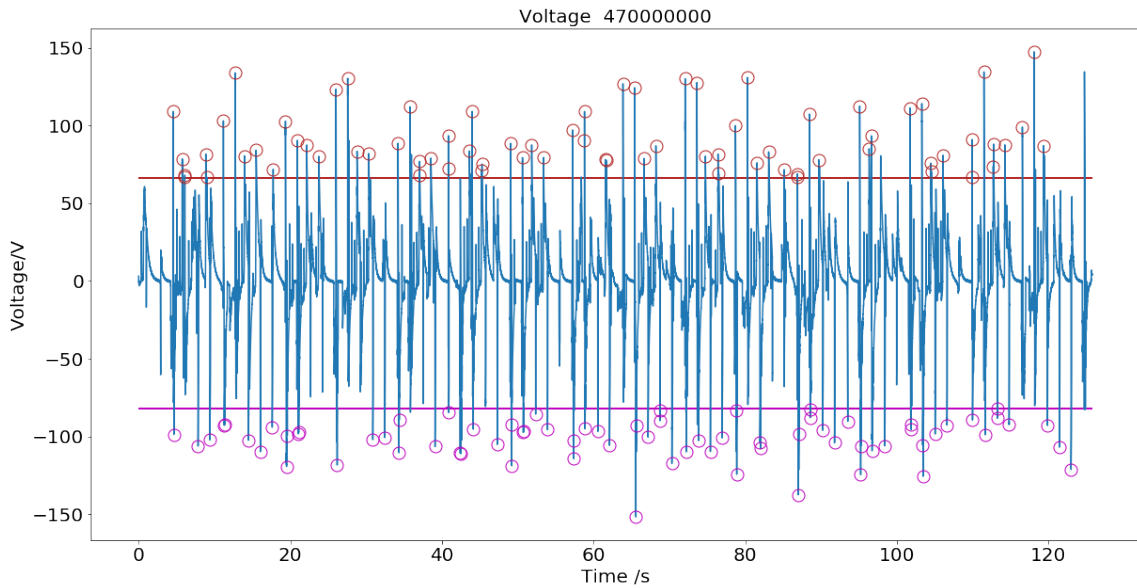


FIGURE 3.5: Threshold lines and selected peaks for a voltage measurement of a TENG, with a load of 470 M Ω .

3.4 Deposition with Spin Coating

The chosen deposition technique for the PTFE aqueous solution was spin coating. This is a simple, inexpensive and effective technique to produce very uniform films from solutions, with controllable thicknesses in the range nm - μm . The substrate is fixed onto the sample holder with a low vacuum, the solution is drop casted onto the substrate until it covers its surface, then the spinner chamber is closed and the rotational motion begins (having

the substrate already rotating when dropping the solution to avoid the accelerating phase can also be an option). First, excess material will be discarded from the sample, through droplets formed at the edges that are expelled, due to the rotation centrifugal force and according to the viscous flow of the solution. During the rotation, evaporation of the solvent starts, increasing the viscosity of the coating, hence gradually fixing it onto the substrate. This way, the rotating speed, the time of rotation and the evaporation rate together dictate the thickness of the coating. However, depending on the surface tension, viscosity of the solution and rotating speed, there can be a non uniform coating thickness between the borders and the center of the sample.

Meyerhofer [88] was the first to model the spin coating process. He inserted the evaporation rate on the previous description, but assuming that the ejection of solution was the dominant mechanism at the beginning of the spin coating process, and that there was an abrupt point after which evaporative thinning became more important. From his model we can write the thickness of the desired thin film as:

$$h_f = \left(\frac{3\eta_0 E}{1(1 - C_0)\eta\omega^2} \right)^{1/3}, \quad (3.1)$$

where η_0 and C_0 are the initial viscosity and concentration of the solution, E is the evaporation rate and ω the angular speed of the spinner. Nevertheless, that abrupt change does not occur for all solutions, and there still is research being done on modelling spin coating. Still, the common practice for achieving the desired film thicknesses is creating a correlation between thickness and spin speed, for each solution, through experimental data, allied with Eq. (3.1).

3.5 Relief analysis with Profilometry

Profilometry is a surface characterization technique, usually used to measure step heights and roughness of surfaces, providing information in Films morphology, thickness and stress, useful from academic research to quality control. The topography can be registered by a stylus in contact with the target surface (stylus profilometry), or by a non contact method, where an image is constructed from the interference pattern between the light reflected by the sample and a reference beam (optical profilometry). In this work, the Bruker DEKTAK XT stylus profilometer was used.

While an optical profilometer has a vertical resolution of angstroms, the stylus profilometer vertical resolution is mainly dictated by the stylus tip shape and diameter (from nanometers to micrometers). As the sample holder moves the surface in the x or y direction (see the pink arrow in Fig. 3.6.a), the stylus tip scans the sample, monitoring the force the surface exerts on the tip, and through a feedback control system, adjusts its vertical position in order to respect the specified value of force. Therefore, smaller stylus tips can detect more variations in the exerted force and execute smaller z displacements, with a better resolution. These vertical displacements relate directly to the height profile of the target surface. The choice of the stylus force (in the order of mg) is important to prevent damage to soft surfaces and prevent tip contamination.

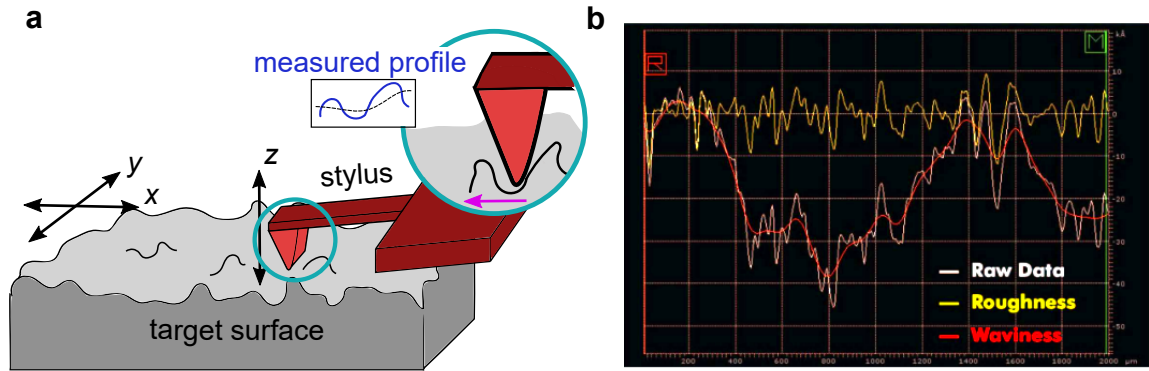


FIGURE 3.6: a) Schematic of the stylus profilometry scanning mechanism; b) Example of a height profile with waviness and roughness (adapted from [89]).

From the height profile, systematic deviations can be eliminated (for instance, tilted stage or substrate) with a baseline correction. If present, the waviness of the surface can also be calculated as a curved baseline, and removed from data, leaving only the roughness, centered on a “zero-level” (see Fig. 3.6.b). Hence, the mean rugosity R_a can be calculated as [89]:

$$R_a = \frac{1}{L} \int_0^L |z'(x)| dx, \quad (3.2)$$

where L is the length (along x) of the measured line and $z'(x)$ is the baseline and waviness corrected height profile along x .

3.6 Fourier Transformed Infrared Spectroscopy

A useful technique to analyze qualitatively and quantitatively the composition of organic compounds is the Fourier Transformed Infrared Spectroscopy (FTIR). This type of spectroscopy explores the vibrational modes of chemical bonds within each molecule to produce a unique spectrum, that allows the identification of the samples composition and concentration.

A molecular energy state depends on the potential energy of the electrons in the molecule (their electronic state), the vibrational energy the bonds have, and the rotational and translational energy of the molecule itself. Each covalent bond possesses a natural vibrational frequency, depending of the mass of the bonding atoms and the elastic force (strength) of the bond. Typically, this frequency is between 10-100 THz, corresponding to infrared radiation. When radiation of that frequency interacts with the molecule, it cannot excite the electrons to more energetic electronic states, but can excite the molecule to a higher vibrational state. This absorption leads to a light intensity drop at the detector of the FTIR device, so that, sweeping through a range of infrared frequencies, a spectrum is constructed.

The samples can be measured in transmission mode, where the absorption will depend on the sample thickness, or in reflection mode. While the first is able to produce high quality spectra, care must be taken on sample preparation, since near all incident light can be scattered or absorbed if the sample is too thick. On the other hand, the Attenuated Total Reflectance (ATR) mode enables the interaction of light with only the sample surface, allowing for a more reproducible, faster and simpler measurement, for a wider variety of materials.

Typically ATR devices possess a crystal of high refractive index against which the sample is pressed, as represented in Fig. 3.7. The incident beam of light is directed towards the surface of the sample, and suffers total reflection inside the crystal until it is gathered by the detector. In each reflection, the evanescent wave produced at the interface penetrates up to a few micrometers into the sample. Increasing the number of reflections and the penetration depth (that depends on the incident light frequency), the detected beam is more attenuated. Typically, it is not the light frequency that is represented on the x-axis of spectra, but instead the spatial frequency or wavenumber, the number of light cycles (number of wavelengths) per unit distance. For infrared light between 10-100 THz, the wavenumbers are $334 - 3334 \text{ cm}^{-1}$ (wavelengths of $\approx 30 - 3 \text{ }\mu\text{m}$).

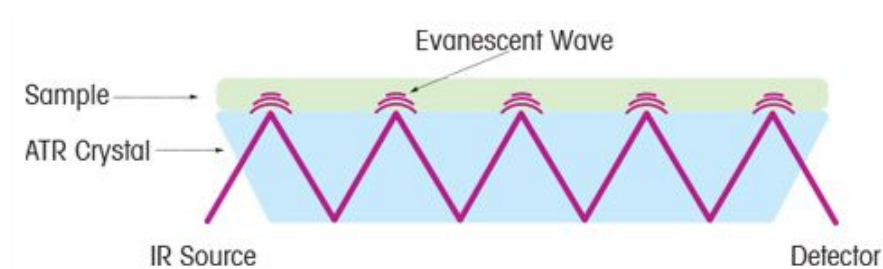


FIGURE 3.7: FTIR-ATR working mechanism, showing the multiple reflections of incident light and the evanescent wave responsible for light attenuation at the detector. Adapted from [90].

3.7 Scanning Electron Microscopy

Scanning Electron Microscopy (SEM) is an imaging technique that takes advantage of the high resolution provided by electron scattering on a sample surface. In a typical SEM setup, a beam of electrons is accelerated towards the sample, and used to raster scan the surface of the sample, interacting with its atoms and producing secondary/backscattered electrons or even X-rays, that are directed to a detector. Contrary to an optical microscope, resolution ($\sim 1\text{-}20\text{ nm}$) and magnification are not limited by lenses size, defects or diffraction, but mainly by the spot size of the electron beam that is scanning the surface, tunable by the magnetic lenses.

Secondary electrons are the result of inelastic scattering on the sample surface, possessing therefore low energy. Zones of high relief will emit, per unit area of the detector, more electrons, resulting in brighter zones, while flat zones of the sample will appear darker. This way, topographical information is obtained from the surface. On the other hand, backscattered electrons, as the name implies, have a higher penetration depth and are elastically scattered by more profound zones of the sample. Therefore, the higher the mean atomic number of a certain portion of the sample, the more backscattered electrons will be produced, hence, a brighter zone will appear on the image. Finally, the electrons can excite the atoms on the sample, leading to the emission of X-rays upon de-excitation that give information as to the elemental composition of the area under analysis: sometimes referred as a different technique, by the name of Energy Dispersive Spectroscopy (EDS).

Chapter 4

Poly(tetrafluoroethylene) thin films deposition and characterization for triboelectric nanogenerators

Poly(tetrafluoroethylene) (PTFE) is a fluoropolymer of low surface energy, hydrophobic and antiadherent, most known as Teflon® (registered by DuPont in 1946). Those properties create the challenge of dispersing it on solution and spin coat onto any substrate, an important knowledge to develop new PTFE based triboelectric nanogenerators. Moreover, the fabrication of PTFE triboelectric layers from aqueous solution would allow for the control of the film properties. Hence, in this chapter a consistent method of fabricating thin films of PTFE from an aqueous solution (DISP-40 665800 Sigma-Aldrich, 60 wt% of PTFE nanoparticles in H₂O, uniformly dispersed by a surfactant), with controllable thickness, onto different electrode materials, is investigated.

4.1 Optimization of substrate material and rugosity

With the first set of samples we intended to explore how the rugosity of the substrate used for the deposition of PTFE samples would affect the PTFE adhesion, and if a more stable and effective TENG could be assembled from them.

The substrates were cut from commercial metallic plates of Cu, Al and Stainless Steel (SS) in squares of dimensions 15 mm x 15 mm. The size of these samples was limited to the diameter of the furnace quartz tube posteriorly used. Part of the substrates were collectively sandblasted at a metal workshop with very thin sand (dimensions unknown).

The substrates were flattened on a mechanical press, cleaned with detergent, acetone and cleaned with ultrasounds for 3 minutes in 70% ethanol and other 3 min in 96% ethanol, then wiped with deionized water and blown dry with N_2 . Three rough and three flat substrates (Al, Cu and SS) were spin coated with the referred PTFE solution at 1500 RPM for 30 s. Then, they were annealed for 30 minutes at 400°C (a value above the crystalline melting point of the resin particles $\approx 337^\circ\text{C}$) in Argon atmosphere, to minimize the formation of oxides between the substrate and the coating that could provoke poor adhesion. Nonetheless, we observed that the copper substrates did in fact become oxidized up to some degree, due to their change in color, as can be seen in Fig. 4.1. To identify the samples, they will be called simply by the name of the substrate if they are flat: Al, Cu, SS. If they have roughness, the suffix “-r” is added: Al-r, Cu-r, SS-r.

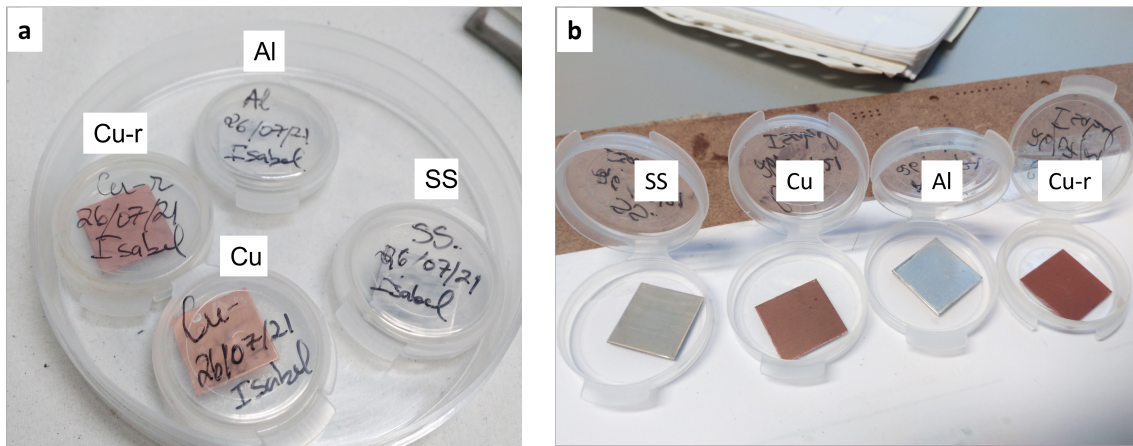


FIGURE 4.1: Photograph of the flat samples and the Cu-r sample: a) before annealing; b) after annealing.

Firstly, the samples of PTFE/metal were measured as part of a contact separation TENG, together with Nylon/Ag. For that, we needed to make the electrical contacts without incurring in the risk of damaging the PTFE layer or oxidating the metal substrate. Therefore, the wires were previously soldered to a long piece of conductive copper tape [with the lowest temperature possible (343°C) to preserve the sheet of paper that protects the glue] (see Fig. 4.2.a). Then, a portion of the rear of the substrate is sanded, to remove residues of annealed PTFE and/or oxides, and only glued to a fraction of the copper tape so that the specific site where the wires are soldered will not be pressed by the contacting force (see Fig. 4.2.b).

With the terminals created, the PTFE/metal and the Nylon/Ag layers were each glued

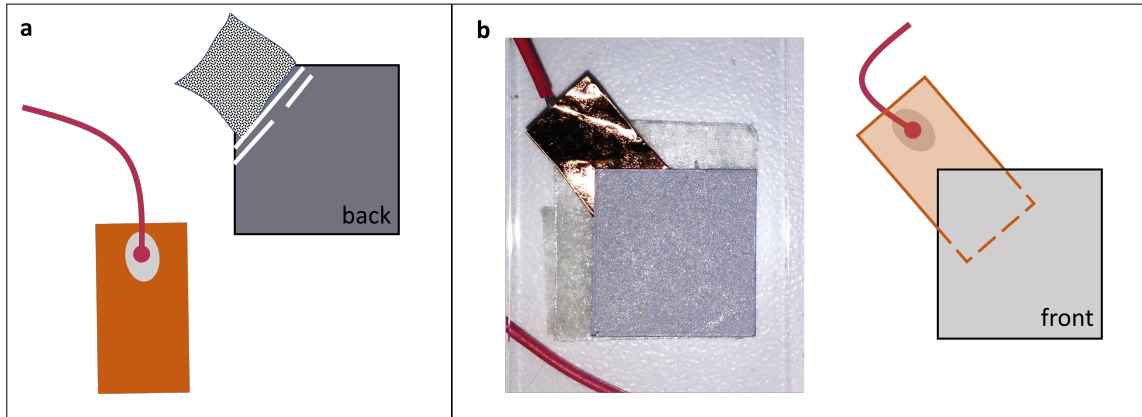


FIGURE 4.2: Special procedures taken to mount a TENG plate from PTFE samples. a) Wire is soldered on one half of a conductive copper tape and one edge of the back of the substrate sanded; b) photography and schematic of the final mounted sample (Al-r), with the tape glued to the sanded edge at the back of the substrate.

to a glass slide, being the first fixed and the second put in motion by the pneumatic linear motor. The motion had a maximum separation between layers of 2.5 cm and period of 1320 ms, that is, a mean velocity of 3.78 cm/s. The samples are contacted and separated by the linear motor, charging the Nylon and PTFE surfaces for 300 s at 470 M Ω and 300 s at 100 Ω - the first resistance to see the voltage increasing, the second to allow the induced charge to establish at the electrodes. Note that these samples, as mounted with copper tape, under this high amplitude motion, did not support isolated, thick and heavy wiring. Therefore, each TENG was connected directly to the Box of Resistances and the Electrometer, without the Commutator, to allow the shortening of the cables and their enclosure on a Faraday cage, attempting to minimize external interferences. Then, the resistance response of the samples was evaluated, measuring the current flowing and the voltage drop at the load as the triboelectric layers were contacted and separated. Due to the compressing/decompressing air cycle of the pneumatic motor, each measurement lasted 120 s.

PTFE sample on:	V_{OC} /V	I_{SC} /nA	P_{max} /nW
Al-r	0.6 ± 0.1	75 ± 9	17 ± 2
Cu-r	0.45 ± 0.05	43 ± 2	15 ± 2
SS-r	0.61 ± 0.05	122 ± 14	26 ± 5
Al	1.3 ± 0.1	212 ± 18	166 ± 8
Cu	0.35 ± 0.05	20 ± 2	7.1 ± 0.7
SS	1.5 ± 0.2	224 ± 18	162 ± 8

TABLE 4.1: Open circuit voltage, short circuit current and maximum power for different substrates, with and without rugosity.

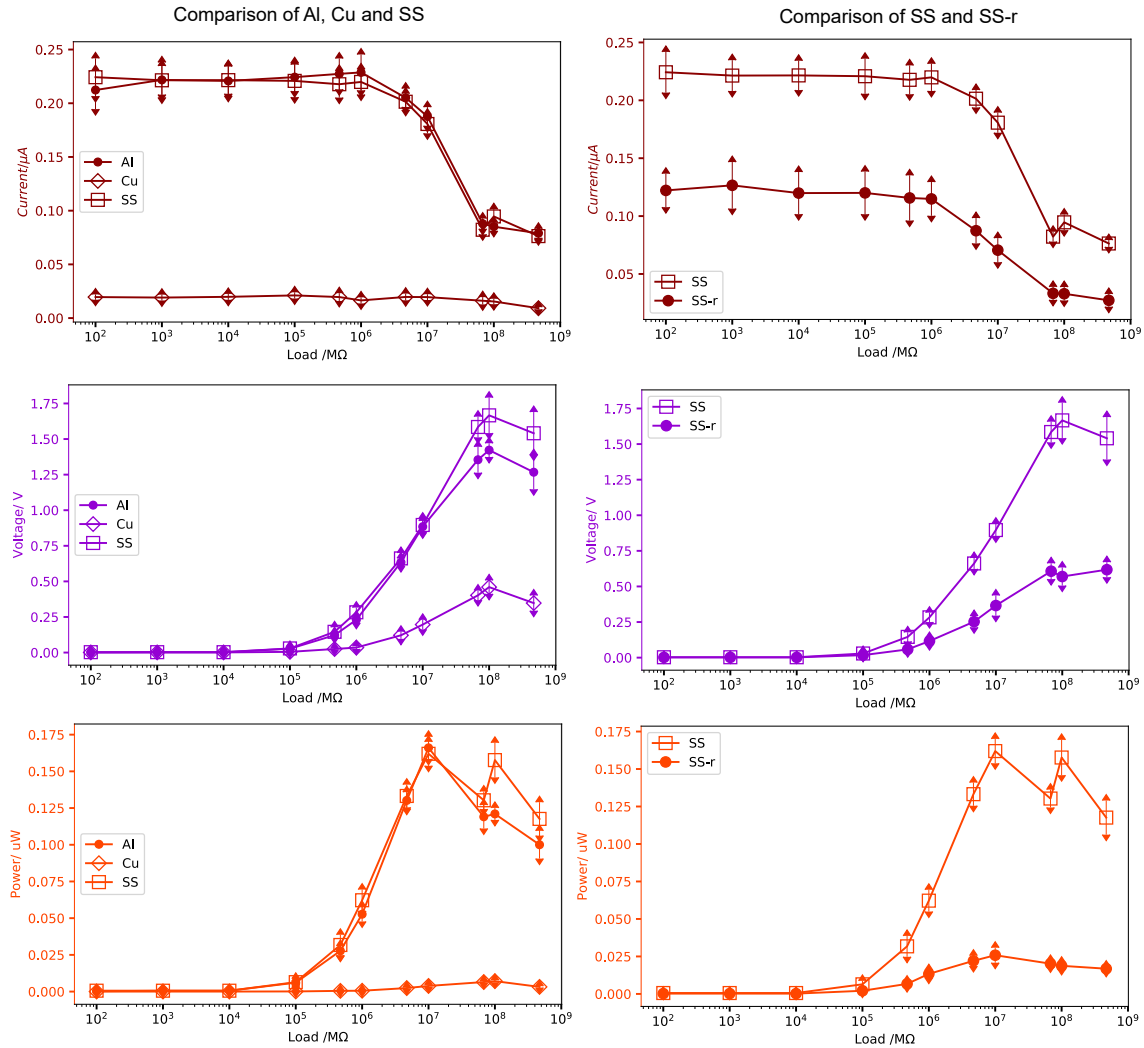


FIGURE 4.3: IVP curves of the TENGs made with the flat substrate samples, on the left, and for the flat and rough substrates samples SS and SS-r, on the right.

From the two types of substrates, flat and rough, the flat substrates presented higher V_{OC} , I_{SC} and P_{max} , excepting for the substrates made of copper (see Table 4.1 and Fig. 4.3). In that case, the TENG made with Cu-r in fact had better results than the one made with flat Cu. Between stainless steel and aluminium, SS proved to be slightly better than Al (see Fig. 4.3), a difference more accentuated on the rough substrates. The optimum resistance was $1 M\Omega$ for all samples with substrates of aluminium and stainless steel, and $100 M\Omega$ for all substrates made of copper.

In general, the outputs were much lower than the reviewed TENGs in section 2.4.2, for several reasons: first of all, we had a very small area of contact, limited by the PTFE samples size. Secondly, the period of 1320 ms (frequency of 0.76 Hz) allied to a maximum distance between layers of 2.5 cm resulted in a very small contact/separation velocity -

an important parameter as it will become more clear on Chapter 6. In fact, in the reviewed literature presented on Table 2.4, all dry tests had a smaller motion amplitude and a higher frequency, and while the first one would not be so easy to reduce in our setup, we could have easily made the period smaller for all tests. Lastly, since reports have shown, for PDMS and PTFE, that output should increase with the thickness on the range of μm [91, 92], the thickness of the PTFE film could have been too small comparing with commercial PTFE films widely used in TENGs ($\sim 10 \mu\text{m}$ thick). This was a big motivation to perform a thickness study for our PTFE solution, in an attempt to achieve thickness up to the tens of μm .

It was surprising the low output obtained with the rough substrates, since it was expected PTFE to be more adhered and consolidated on a rough surface. Additionally, after the tests with the rough substrates, the Nylon sheet showed small, dot marks from being pressed against the rough samples. This suggested that there could be uncovered parts of the substrate, or in other words, the rugosity was so high that for the used conditions of spin coating, the quantity of PTFE was not enough to form a thin film on top of the substrate.

4.1.1 Substrate rugosity characterization

To probe how the rugosity affected the film, the 3D relief of rough substrates was measured with the Bruker DEKTAK XT profilometer, on a square of $2 \text{ mm} \times 2 \text{ mm}$. 200 lines separated of $10 \mu\text{m}$ were acquired, each for the duration of 30 s. The height range was $65.5 \mu\text{m}$ and the stylus (with radius of $2 \mu\text{m}$) applied a force of 3 mg on the film.

From the 3D maps in Fig. 4.4 we see that the affected areas (either above or under the zero level) have a decreasing size from Al-r, to Cu-r, to SS-r. Also, the mean roughnesses are not the same on all substrates, but instead follow a clear decreasing order from Al-r, to Cu-r, to SS-r. Since the same sandblasting process affected the three metals, the different rugosities must be attributed to the increasing hardness, in that same order [93]. Therefore, producing the same rugosity for all metals with mechanical ablation methods should take into account their different hardnesses.

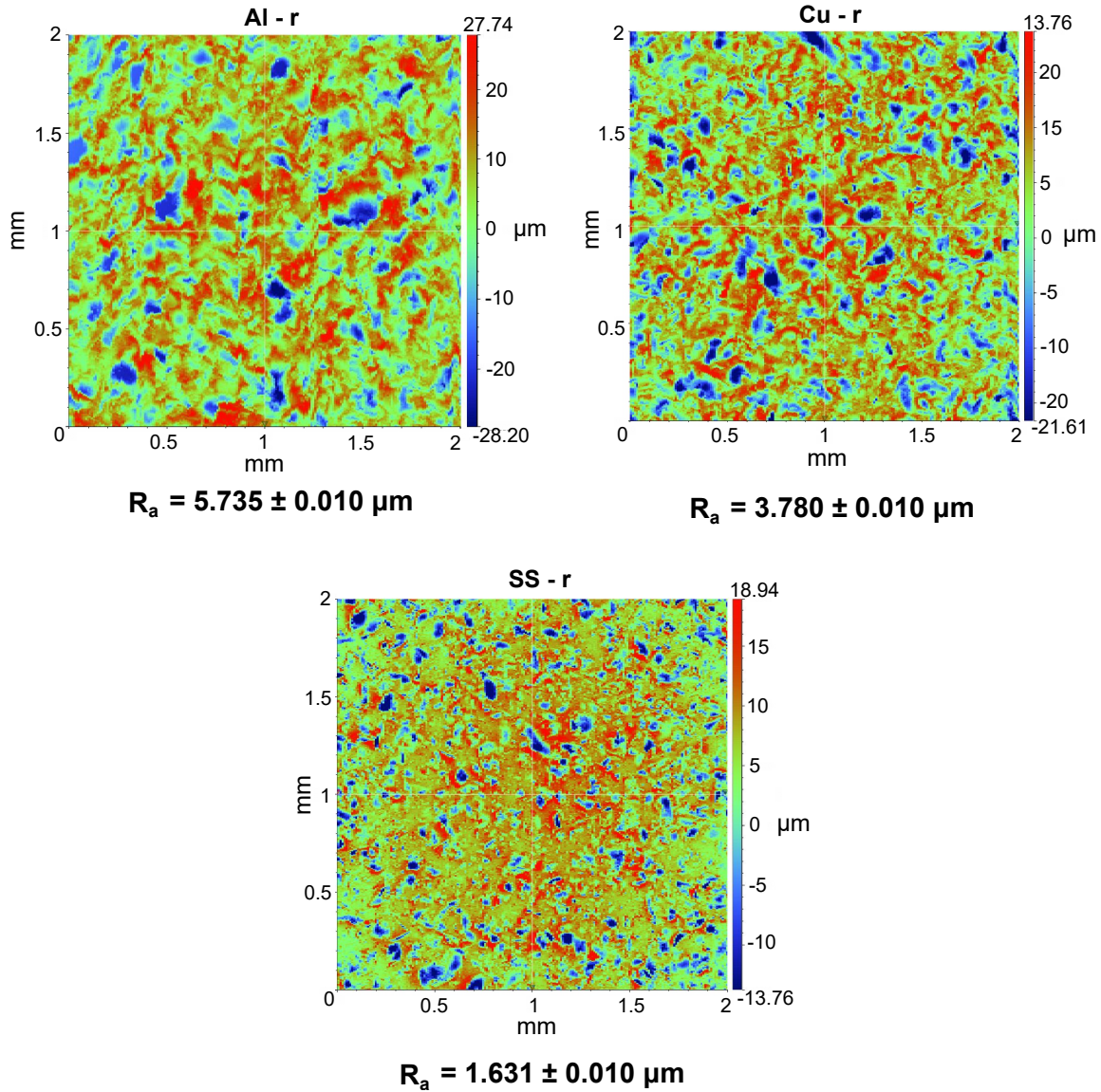


FIGURE 4.4: Rugosity maps for the Al-r, Cu-r and SS-r samples, with the corresponding mean roughness. The colorbar shows the height relative to a calculated zero level that minimizes all the differences of height to the level.

4.1.2 Chemical composition characterization

We performed Fourier Transformed Infrared Spectroscopy - Attenuated Total Reflectance (FTIR-ATR Perkin Elmer Spectrum BX, spatial frequency from $4000\text{--}200\text{ cm}^{-1}$) on all samples, with the objective of identifying the composition of the coating and understand better the triboelectric performance of the samples. The PTFE spectrum typically has a strong absorption region on the range $1250\text{--}1100\text{ cm}^{-1}$ attributed to C-F stretching [94, 95], and sometimes an overtone of this vibration around 2300 cm^{-1} [96] is detected. According to the reviewed reports, there are two characteristic peaks from stretching, around $1200\text{--}1299\text{ cm}^{-1}$ for asymmetric stretching and 1150 cm^{-1} for symmetric stretching [94, 95, 97].

Peaks around $625\text{--}642\text{ cm}^{-1}$ have been attributed to vibrations of the molecular chain, of helicoidal structure, of crystallized portions of the film [98, 99], while peaks at 556 cm^{-1} are linked to CF_2 rocking [97], and at $502, 512\text{ cm}^{-1}$ to CF_2 wagging and twisting [95, 97]. For a more visual explanation of these vibrational modes, see Fig. 4.5.

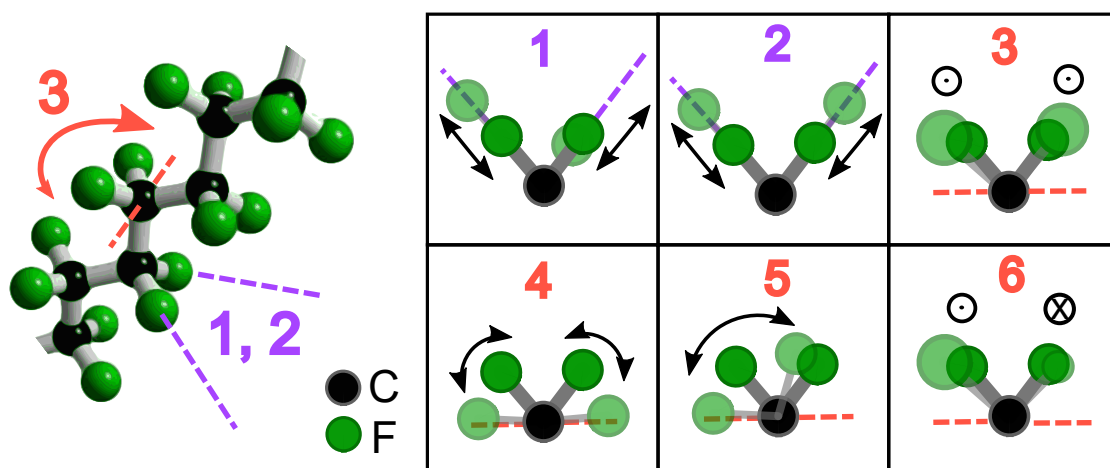


FIGURE 4.5: Vibrational modes of PTFE, most of them identified in the samples: 1) symmetrical stretching: each F atom stretches away and towards the C atom they share, in phase; 2) asymmetrical stretching: each F atom stretches away and towards the C atom they share, in antiphase; 3) wagging: both F atoms tilt along the longitudinal direction of the molecule, towards one or another end of the chain; 4) bending (scissors movement); 5) rocking (tilting in phase); 6) twisting (wagging in antiphase).

The spectra obtained (Fig. 4.6) were processed in essentialFTIR® and compared to a wide database on Open Specy [100], an open source tool to analyze and identify chemical species from Infrared Spectroscopy and Raman Spectroscopy data, comparing them to published spectra. Our data was compared with the work of Primpke *et al.* [101], whose data range was large enough to compare all our peaks. The identification of PTFE was made automatically by Open Specy, that calculates the Pearson's correlation coefficient (ρ) between the peaks in the chosen reference and the peaks of our spectrum. We were able to identify the presence of PTFE on our samples and the molecular vibrational mode at the origin of most of the absorbance peaks, as summarized on Table 4.2.

Besides PTFE, in both spectra was detected the presence of H_2O vapor (noise regions at $4000 - 3400, 2000 - 1300\text{ cm}^{-1}$) and atmospheric CO_2 (peak at 2350 cm^{-1}), since our FTIR-ATR device has no chamber separating the sample from the environment (see the insets of Fig. 4.6). Note that the height of the peak at $\approx 2350\text{ cm}^{-1}$ is comparable to the PTFE fingerprint peaks for rough samples, but much smaller for flat samples. If it was PTFE originated, then for rough samples it should be much smaller as well than the PTFE peaks, therefore it was attributed to CO_2 .

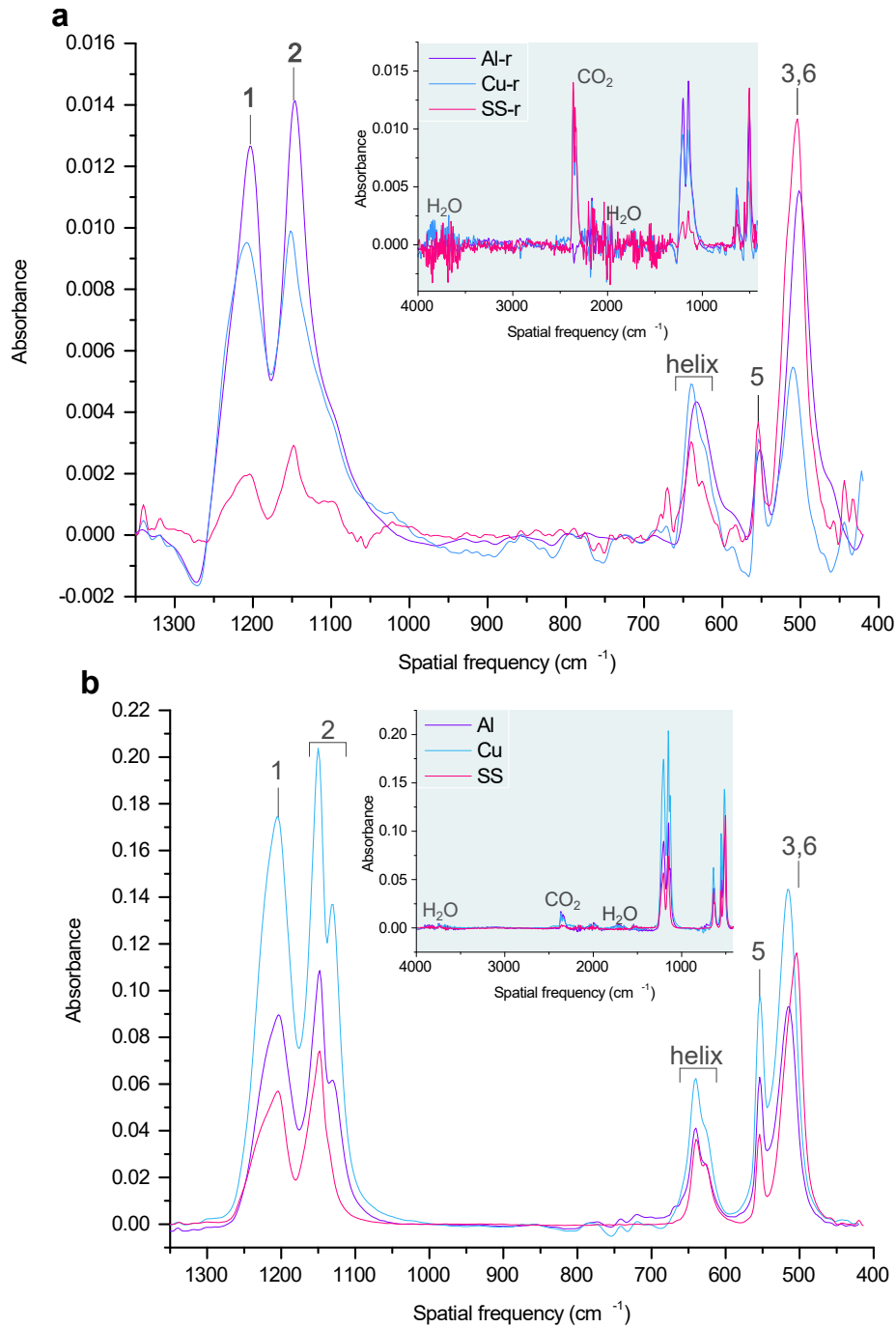


FIGURE 4.6: FTIR spectra for rough (top) and flat (bottom); samples of different substrates. The inset shows the full spectrum, and the main windows is a zoom of the region of interest to PTFE identification, 400 - 1350 cm⁻¹, where the peaks are labeled with the vibration their origin.

Peaks spatial frequency ($\pm 4 \text{ cm}^{-1}$)			Vibrational mode (no.)
Al ($\rho = 0.84$)	Cu ($\rho = 0.83$)	SS ($\rho = 0.86$)	
1204	1205	1205	asymmetrical str. (1)
1148	1150	1148	symmetrical str. (2)
1131	1131	—	
640	640	640	helix structure
—	—	627	
553	554	554	rocking (5)
514	516	504	wagging, twisting (3,6)
Al-r ($\rho = 0.95$)	Cu-r ($\rho = 0.82$)	SS-r ($\rho = 0.56$)	
1203	1208	1209	asymmetrical str. (1)
1146	1152	1148	symmetrical str. (2)
633	639	639	helix structure
552	554	554	rocking (5)
501	510	504	wagging, twisting (3,6)

TABLE 4.2: Spatial frequencies of the infrared spectra peaks, detected by FTIR-ATR, and their corresponding vibrational modes, for the different substrate material and rugosity samples. The Pearson's correlation coefficient (ρ) between our peaks and the reference is indicated after the name of each sample.

Notice that the absorbance of the rough substrate samples was much lower than the absorbance of the flat samples. Being FTIR-ATR a surface analysis technique, if the surface has irregularities at a smaller scale than the length of the FTIR crystal ($\sim \text{mm}$), the crystal might not touch the PTFE surface in some points, reducing the intensity of the signal detected from PTFE - suggesting again uncovered, steep parts of the substrate. For the same reason, if different surface morphologies exist between samples at the place of contact with the FTIR crystal, then there could be clearances between the prism and the

sample, hence a smaller absorbance will be detected [102]. Yet another reason for disparities of peak height between samples can be the clamping force applied on each sample compared to its hardness, since that will affect the area of contact between the surface and the FTIR crystal [102]. This can explain why the samples of stainless steel, being the metal whose deformation is more difficult among the tested, consistently showed lower absorbances on the C-F stretching region.

Observing Table 4.2, note that there are differences between samples of the spatial frequencies for each vibration, although the deposited PTFE is the same material, and even from database to database, differences were found. If a pressure is applied on the PTFE molecules, their frequencies of vibration will be deviated [103, 104]. Hence, these spectral changes can also be originated by differences in the clamping force or morphology between the sample and the FTIR prism.

4.1.3 Coating quality and uniformity

All three rough samples and the SS flat sample were analyzed by Scanning Electron Microscopy (SEM Quanta 400 FEG ESEM/EDAX Genesis X4M) using an accelerating voltage of 10 kV. Images of Z-contrast were taken at 200x, 1000x, 5000x and 10000x, and are presented in Figs. 4.7 for the rough samples and 4.8 for the SS flat sample.

The bright zones represent the substrate, while the darker zones are the PTFE coating (lower average Z than the metallic substrate). On the rough samples images (Fig. 4.7), the PTFE is clearly wetting the rugosity, as shown by the gradient of grey over the surface in SS-r, and near each substrate mountain, that represent a mixture of the mean Z value of the substrate and PTFE. However, the PTFE did not coat any rough substrate completely, as parts of it are always visible.

While on Al-r and SS-r the images of 10000x magnification show spherical nanometric structures of about 200 nm of diameter, on Cu-r sample the coating was composed of fibers. There is no evident reason for this, although it could be result of a more effective annealing on the Cu substrate, that merged the spherical particles together, due to the differences in specific heat and thermal conductivity of copper relative to aluminium and steel. For this reason, in Al-r and SS-r several cracks were observed, while on Cu-r they were observed ruptures on its fibrous layer. These cracks most certainly occurred due to the contact separation cycles when testing the triboelectric performance of the samples.

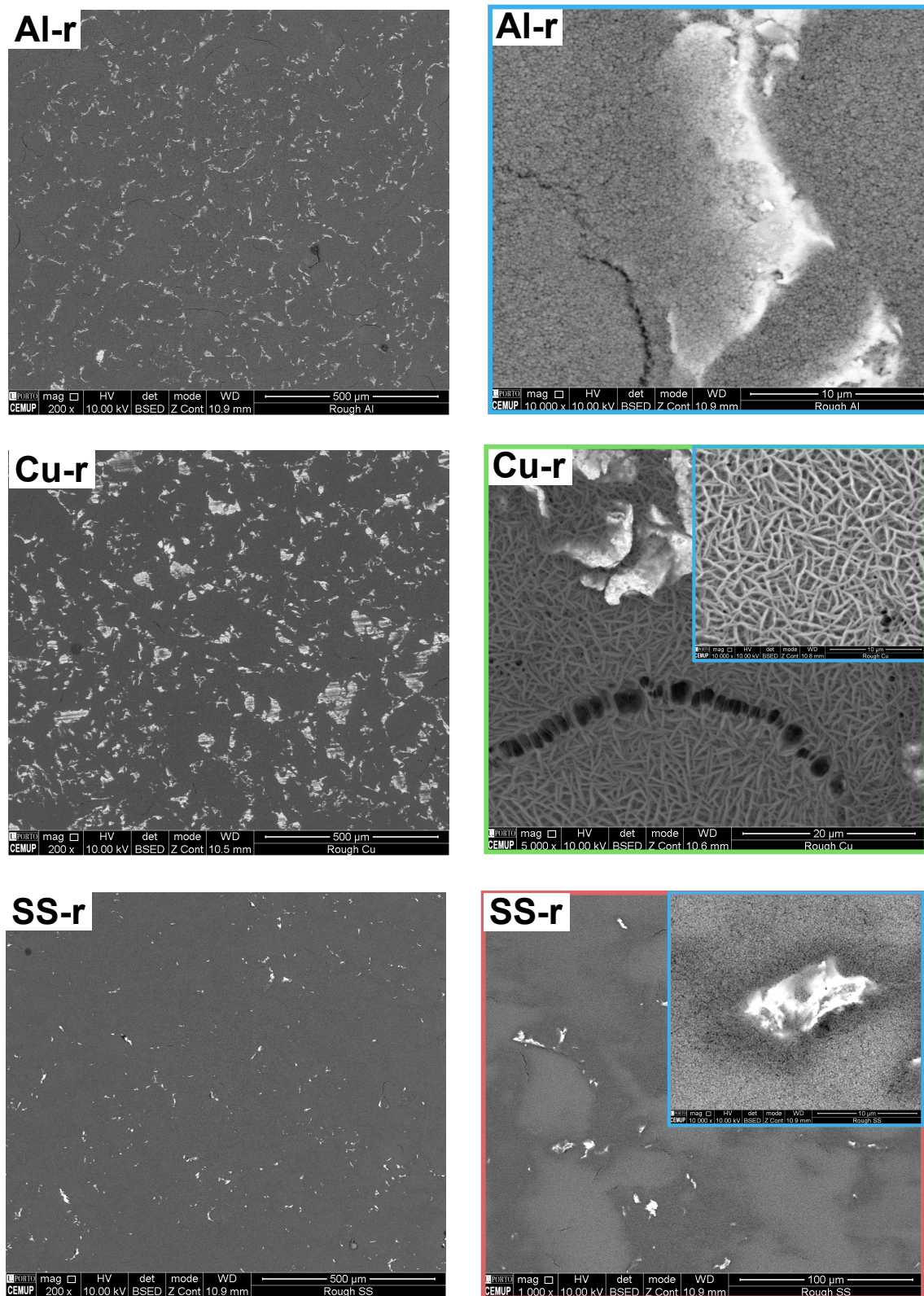


FIGURE 4.7: SEM images of the rough substrate samples with Z-contrast and voltage of 10kV. The colors represent the magnification: 200x if no color is present (scale 500 μm); salmon for 1000x magnification (scale 100 μm); green for 5000x magnification (scale 20 μm); blue for 10000x magnification (scale 10 μm).

The scenario is completely different for the flat SS sample. It showed a uniform coating with no substrate visible (see Fig. 4.8), also composed of agglomerated spheres of ~ 200 nm of diameter. This is the diameter of the particles suspended on the PTFE DISP-40 solution used for the coating. With the actual data, it is unclear to what extent the annealing affected the melting and agglomeration of these particles for the SS and the Al substrates.

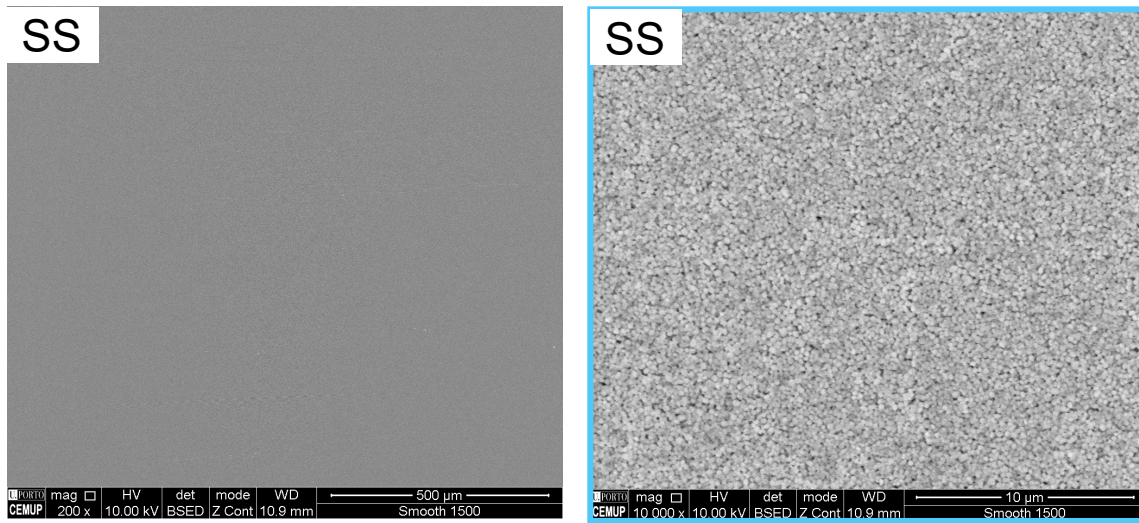


FIGURE 4.8: SEM images of the SS sample with Z-contrast and voltage of 10 kV. The colors represent the magnification: 200x if no color is present (scale 500 μm); blue for 10000x magnification (scale 10 μm).

4.2 Calibration of thickness and spin coating speed

Since the flat SS substrate was the one that showed the best results when incorporated in a TENG, a thickness study was done in this substrate. Starting with the same cleaning process described in the previous section, four samples, let them be sample 1 to 4 (see Fig. 4.9), were fabricated by spin coating with speeds 500, 750, 1000 and 1250 RPM, respectively, spinning for 30 s. The same area at the top right corner of each sample was protected with tape during the coating process, so that, after its removal, a step between the substrate and the film was available for thickness measurement. Afterwards, the samples were annealed at the same conditions as before: Ar atmosphere at 400°C for 30 minutes. After this process, a difference in thickness for sample 1 was already visible due to the different camera angle needed to capture the brownish color the other samples displayed (see Fig. 4.9).

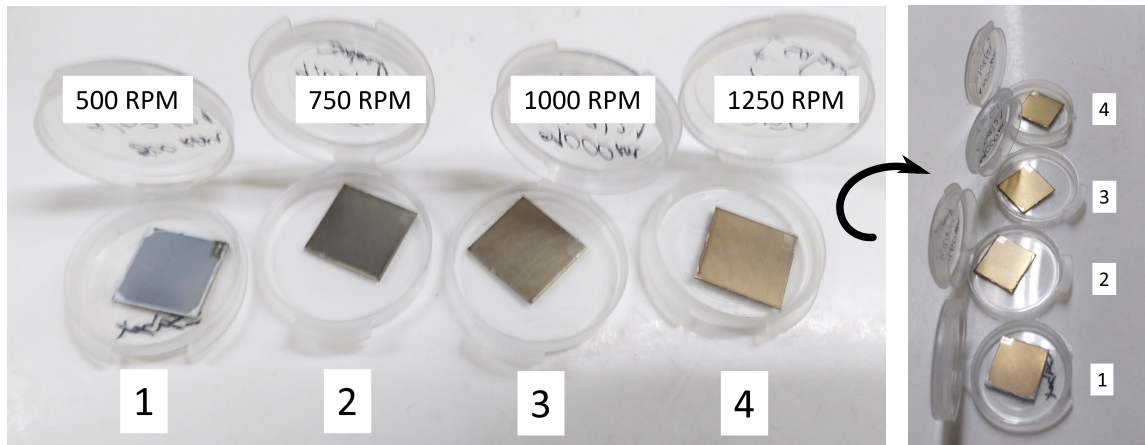


FIGURE 4.9: Photographs of the samples fabricated with different spin coating speeds, after annealing, at different angles. Note the top right corner without PTFE coating due to the tape protection during spin coating.

These samples followed the same wiring method as the samples on section 4.1.2, mounted with copper tape. Hence, they were also connected directly to the Box of Resistances and the Electrometer, with very short cables all inside a Faraday cage. However, the triboelectric layers were charged more thoroughly than before, for ≈ 1400 s at 100Ω . The resistance response was then measured, contacting the triboelectric layers for the same amplitude and period of motion used in the previous samples. The optimum resistance was $68 \text{ M}\Omega$ for samples 1, 2-4 and $100 \text{ M}\Omega$ for sample 3. The open circuit voltage, short circuit current and maximum power are presented on Table 4.3 and Fig. 4.10.

The first observation concerns the values of the three electrical quantities analyzed, that are, in overall, higher than for the previous samples. This was in line with the expected thicknesses to be higher than the last study, since all these tested RPM were smaller than the 1500 RPM used before. However, it is in fact strange that no clear tendency was found in samples expected to have increasing thicknesses from 1250 RPM to 500 RPM . Even if the rotation speed was not actually affecting the thicknesses significantly, there is no evident reason why the sample 3 (1000 RPM) should have higher output than the sample 2 (750 RPM), while being similar to the output of sample 1 (500 RPM). Looking to the full resistance response (represented in Fig. 4.11), we see that samples 1 and 3 form a group with roughly the same output, and samples 2 and 4 another group. Note that, for all samples, the current at the highest resistance is not significantly lower than the short circuit value - showing that measurements at higher resistances would help to better define the power curve and the open circuit voltage. As arbitrary as these results might seem, these samples were measured more than once, and still the same behavior, with

similar values, was obtained. A possible explanation could be that the samples had all very similar thicknesses, so that not even one of them distinguished itself from the others. Still, it is curious the reproducibility of such an unexpected behavior.

Sample	RPM	V_{OC} /V	I_{SC} /nA	P_{max} / μW
1	500	3.8 ± 0.6	523 ± 37	1.4 ± 0.2
2	750	2.3 ± 0.1	170 ± 6	0.359 ± 0.008
3	1000	3.0 ± 0.3	548 ± 31	1.36 ± 0.08
4	1250	1.8 ± 0.1	303 ± 18	0.229 ± 0.008

TABLE 4.3: Electrical performance of PTFE samples fabricated with different spin speeds when incorporated on a TENG.

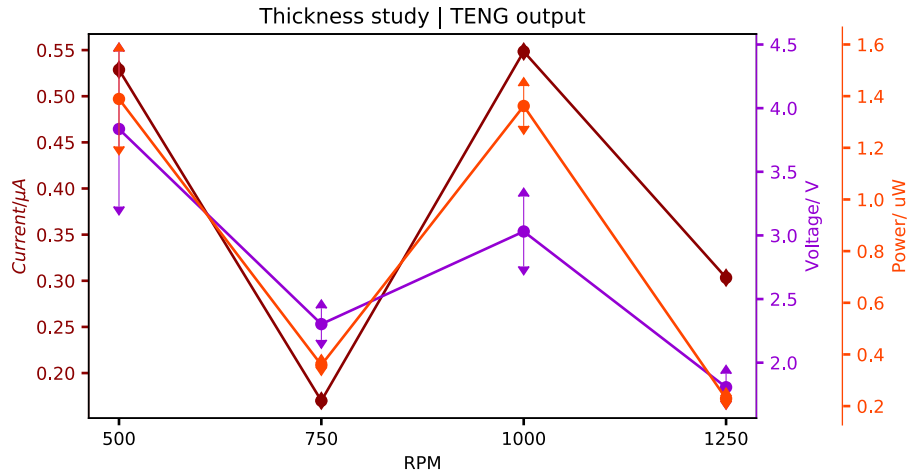


FIGURE 4.10: Graph of the electrical performance of PTFE samples fabricated with different spin speeds when incorporated on a TENG.

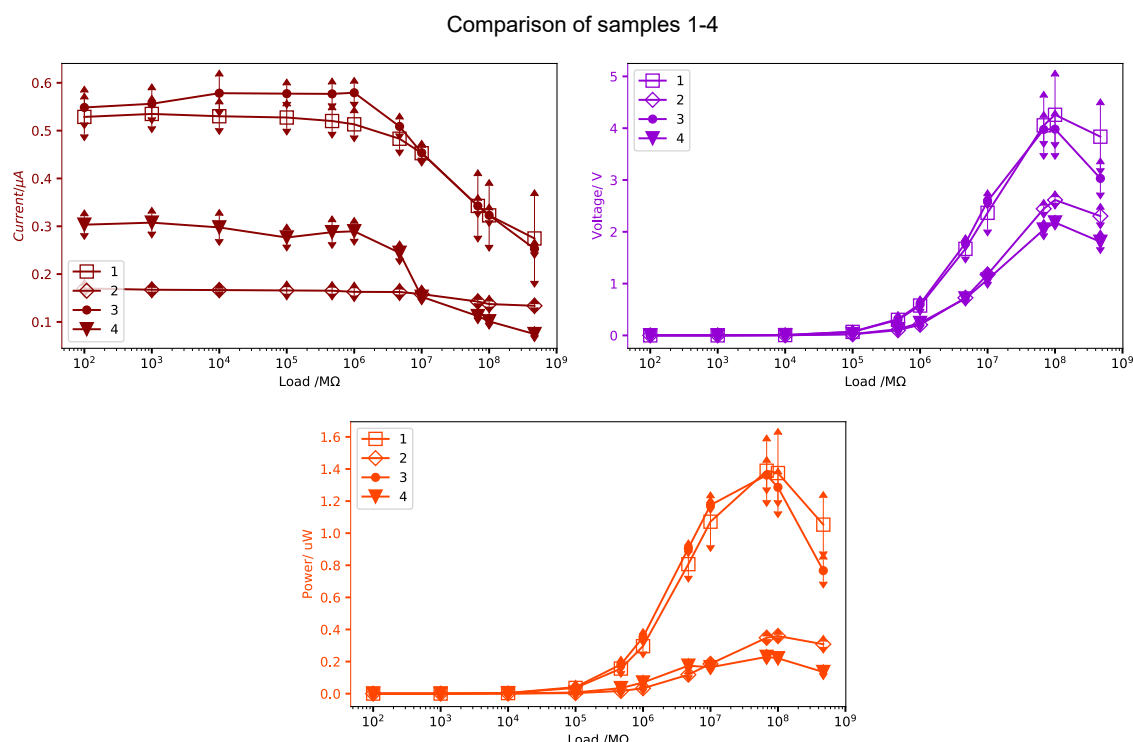


FIGURE 4.11: IVP curves comparing the TENGs output made from the samples 1-4, fabricated with different spin speeds.

4.2.1 Chemical composition

All samples were analyzed with Fourier Transformed Infrared Spectroscopy - Attenuated Total Reflectance (FTIR-ATR Perkin Elmer Spectrum BX, spatial frequency from 4000-200 cm^{-1}), to infer the presence of PTFE and other compounds, if present. The molecular modes detected were the same as the samples from section 4.1.2, with the addition of another CF_2 asymmetric stretching originated peak at 1217 cm^{-1} and a CF_2 symmetric stretching at 1119 cm^{-1} , both for sample 3 (1000 RPM), that had not been detected before near these values of spatial frequency (see Table 4.4). A bad coupling between the surface and the crystal may have originated the relatively low signal for samples 2 and 3 (see Fig. 4.12), although more information is needed to confirm this hypothesis, for instance, repeating the measurement on other parts of the film.

Peaks spatial frequency($\pm 4 \text{ cm}^{-1}$)				Vibrational mode (no.)
1 ($\rho = 0.82$)	2 ($\rho = 0.75$)	3 ($\rho = 0.57$)	4 ($\rho = 0.83$)	
—	—	1217	—	asymmetrical str. (1)
1204	1200	1203	1204	
1147	1144	1146	1148	symmetrical str. (2)
—	—	1119	1129	
639	639	640	640	helix structure
—	—	—	628	
554	554	554	554	rocking (5)
502	513	514	515	wagging, twisting (3,6)

TABLE 4.4: Spatial frequencies of the infrared spectra peaks, detected by FTIR-ATR, and their corresponding vibrational modes, for the samples of different thicknesses. The Pearson's correlation coefficient (ρ) between our peaks and the reference is indicated after the name of each sample.

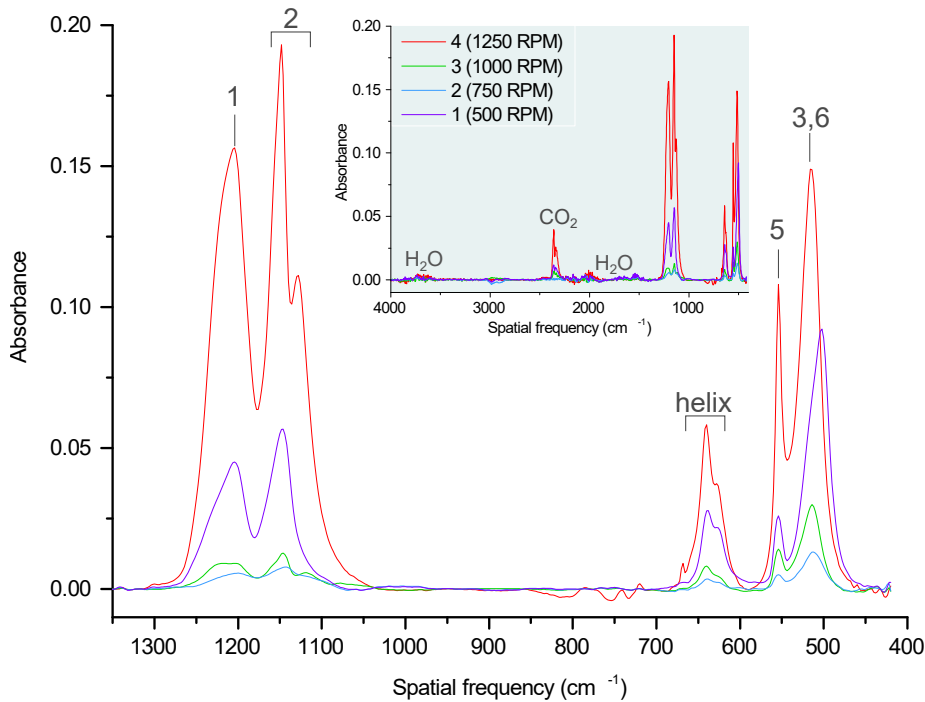


FIGURE 4.12: FTIR spectra for samples fabricated with different coating speeds. On the main window there is a zoom of the region of interest to PTFE identification, $400 - 1350 \text{ cm}^{-1}$, with labeled peaks, while the inset shows the entire obtained spectra ($400 - 4000 \text{ cm}^{-1}$).

4.2.2 Uniformity and thickness evaluation

To characterize the thickness of the film, the gap between the substrate and the top of the film was measured by profilometry, taking into account possible border effects. The lines were measured perpendicularly to the interface (3-5 lines per sample), along 2-4 μm , for 30 s each, in the 65.5 μm height range and with a 3 mg force. We observed that the stylus recorded an accentuated height increase before it fell down to touch the substrate (shown in Fig. 4.13). In reality, although the coating spread over the tape on the corner of each sample during spin coating, the tape acted like a barrier to be surpassed, modifying the morphology of the film at the corresponding interface.

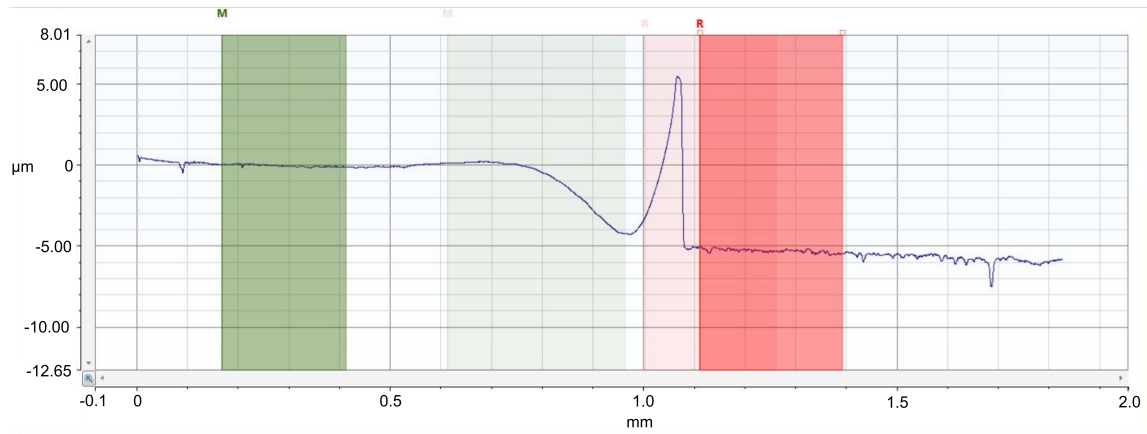


FIGURE 4.13: One of the steps measured by profilometry to calculate the thickness of the PTFE films for sample 1 (500RPM).

The thicker the sample, the more difficult it was to obtain an accurate measurement of the thickness. The mean values of the measurements were calculated (see Table 4.5) and were fitted to a power of the angular rotation speed $h \propto \omega^{2/3}$ (see Table 4.6 and Fig. 4.14). The thickness increases, as expected for smaller spin coating speeds. Still, a proper real calibration would need more thicknesses to be validated.

Sample	RPM	$d_{\text{PTFE}} / \mu\text{m}$					$\overline{d_{\text{PTFE}}} \pm \sigma$
1	500	3.963	5.238	4.950	4.048	4.439	4.5 ± 0.5
2	750	2.676	2.461	2.219	2.861	-	2.5 ± 0.2
3	1000	2.226	2.100	2.253	-	-	2.19 ± 0.07
4	1250	1.942	1.874	1.980	-	-	1.93 ± 0.04

TABLE 4.5: Several measurements of thickness, from different regions of the same step, of the PTFE samples on SS.

Equation	$m \pm \Delta m$	$\frac{\Delta m}{m} (\%)$	$b \pm \Delta b$	$\frac{\Delta b}{b} (\%)$	R^2
$d_{PTFE} = m \left(\frac{1}{\omega^{2/3}} \right) + b$	361 ± 66	18%	-1.4 ± 0.7	57%	0.94

TABLE 4.6: Fitting parameters for the dependence of the PTFE coating thickness on spin coating speed.

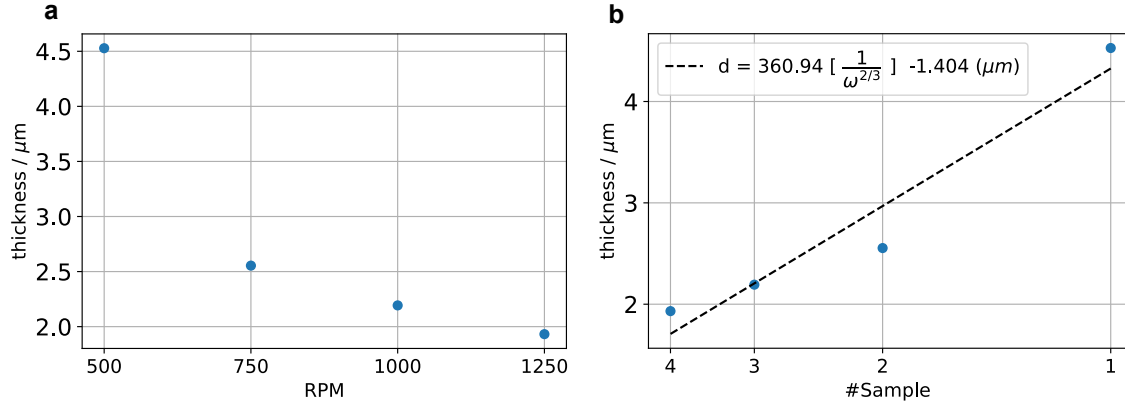


FIGURE 4.14: a) Thicknesses measured by profilometry and the correspondence to the spin speed of each sample; b) Fit of the thickness as function of the inverse square root of spin coating speed.

However, topographic SEM images for sample 1 showed the profilometer had damaged the surface, exerting too much force on the film (see Fig. 4.15.a). Therefore, since the same stylus force was used for all measurements, the thickness is in fact increasing for samples fabricated with lower spin speed, although the real values of thickness are larger than the recorded on Table 4.5 and Fig. 4.14.

Observing the topology of sample 1 in Figs. 4.15.b,c, there is a good film uniformity, although the existence of a higher border near the edge of the step was confirmed. Moreover, there is a lateral division on the coating (signaled by the red arrow in Fig. 4.15.a), as if two layers of coating were applied. In fact, this might be a result of the placement of the tape during spin coating, so that the ‘‘bottom layer’’ corresponds to the thickness of the tape, and the ‘‘upper layer’’ the accumulation of material due to the border effect. This effect prevents the measurement of thickness from SEM images, since the value would be greatly overestimated. The spherical agglomerates were also observed for 10000x magnification, similarly to the samples of section 4.1.2 (evidenced in Fig. 4.15.c).

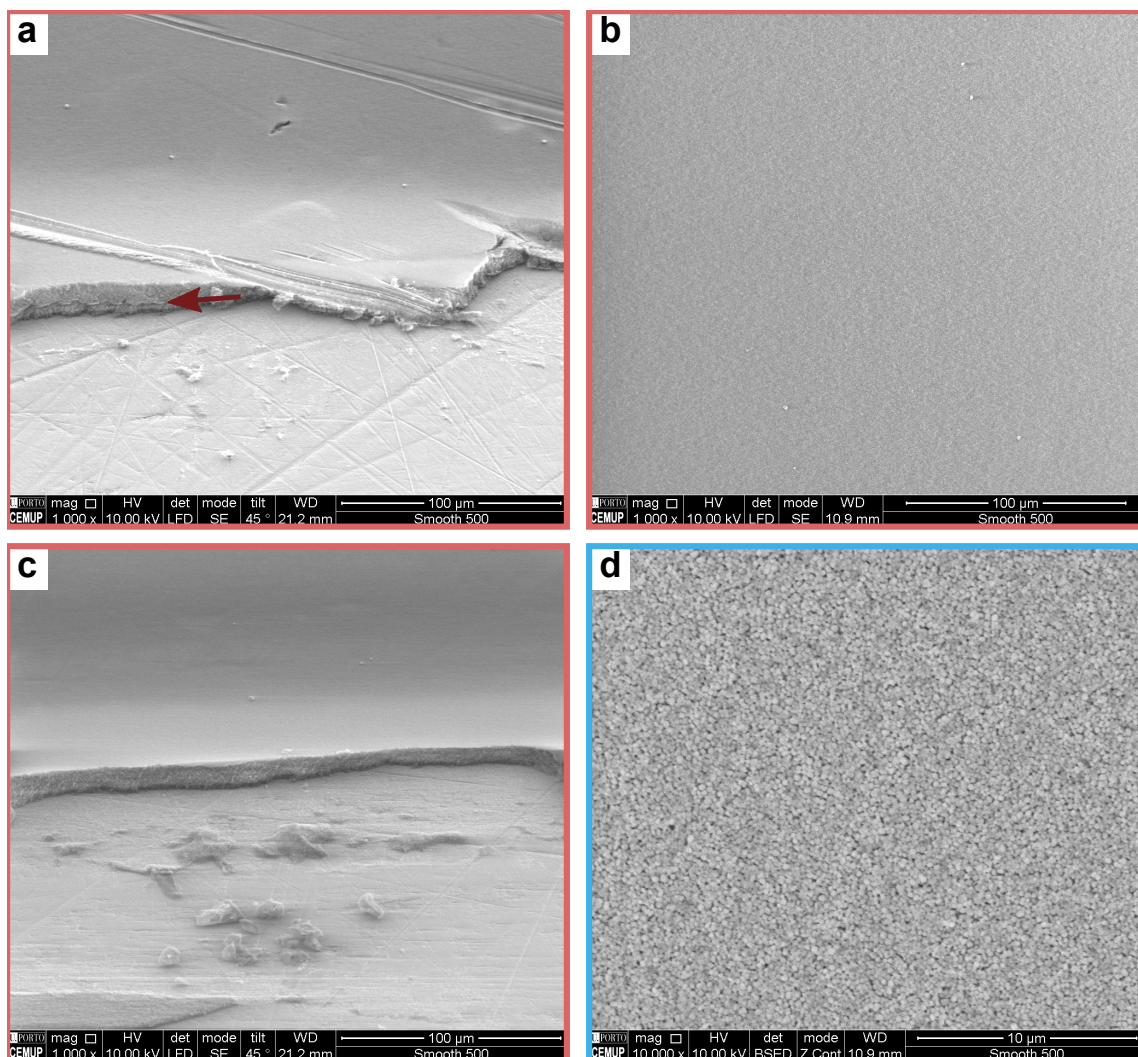


FIGURE 4.15: SEM images for sample 1 (500 RPM), obtained with voltage of 10 kV. The colors stand for magnification: salmon for 1000x (scale of 100 μm) and blue for 10000x (scale of 10 μm). a) Secondary electrons image showing the profilometer lines, taken at a 45° angle; b) secondary electrons image if the coating; c) secondary electrons image showing the step, at a 45° angle; d) Z contrast image evidencing the spherical agglomerates of PTFE.

4.3 Summary

Although the TENGs for the flat and rough samples showed small outputs, it was possible to identify the best substrate from the tested samples to be flat stainless steel. This sample had a uniform coating of PTFE film, composed by an agglomeration of spherical particles from the solution that originated it.

The high rugosity of the rough substrates led to the deposition of a discontinuous PTFE film, with uncovered parts of the substrate. This was reflected in the low output of the TENGs made with these samples and the small absorbance of infrared light detected,

comparing to the flat samples.

Our study of thickness revealed the damage than PTFE thin films can suffer from stylus profilometry and the importance of testing different characterization techniques to verify the results. The thickness of the films increased with the reduction of spin rotation speed, nonetheless, a calibration curve could not be constructed with the information available. Quantifying the thickness of the films would have been important to understand the TENG output unexpected results. These were the first steps towards the deposition of controllable thickness PTFE thin films from aqueous solution for application on triboelectric nanogenerators, which served, above all, to define what the next steps will and will not be.

Along with this attempt of fabricating PTFE thin films, TENGs with commercial PTFE films were also tested, having showed better results in terms of current, voltage and power. Therefore, we focused on the optimization of a device assembled from a commercial PTFE film, that could be translated into other devices as well, as it will detailed in the next chapter.

Chapter 5

UL-TENG output characterization and optimization

5.1 Our device: the UL-TENG

The UL-TENG (represented in Fig. 5.1) is composed of two generators at opposite ends of a plane track and rolling spheres (of stainless steel, diameter 12 mm), that are responsible for closing the mobile, rotating part of each generator. The triboelectric generators are identical and consist of Ag electrodes screen printed on commercially obtained sheets of Nylon 6.6 (thickness of 17 μm) and PTFE (thickness of 50 μm), with dimensions 2.5 cm x 4 cm (area of 10 cm²). The Nylon sheet is fixed onto the mobile part (see Fig. 5.2.a), and the PTFE sheet onto the static part (see Fig. 5.2.b), so that its adherence to the silver electrode is more protected. On their turn, these mechanical parts and the track are 3D printed in black PLA. The static part of each generator has an angle of 20° with the vertical, so that the mobile part could be at its resting position along the vertical direction, and still be separated from the static part, creating some space to be closed upon contact (see Fig. 5.2.c-d).

In the context of this work, the UL-TENG was modified to allow the study of different track lengths in a fast and efficient way. This was accomplished by creating a locking system with small lateral slits on the track and plates that extended from the back of each generator to fit tightly on those slits (see Figs. 5.2.d-e). Moreover, a small height on the bottom of each static part was added to allow the mobile part to rotate more freely, given that now the generator was not glued at a suitable height, but had to be functional by itself once fitted into the slits.

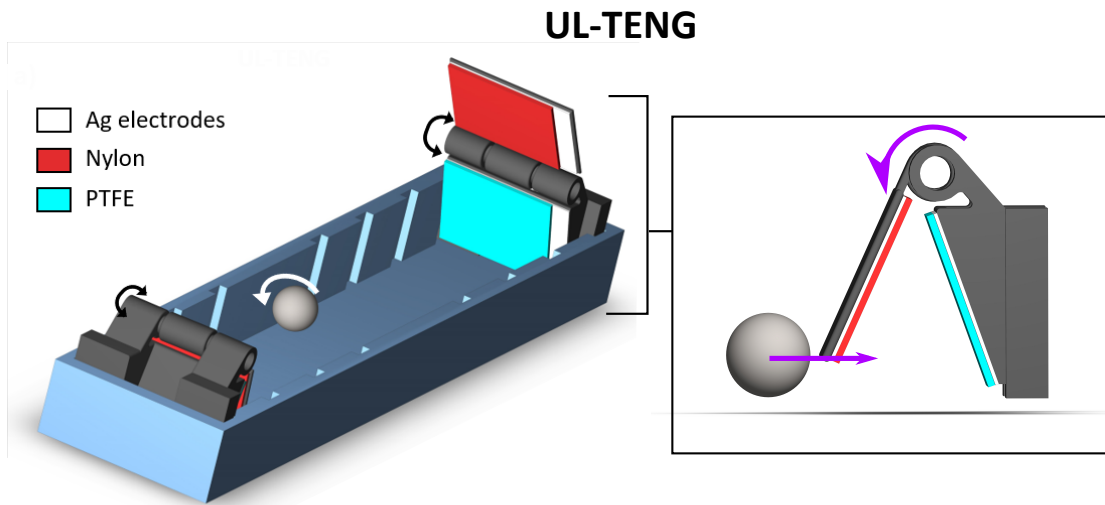


FIGURE 5.1: The UL-TENG on the left. On the right there is a schematic of the closing of the generator placed at each side of the linear track. Images from Solidworks®.

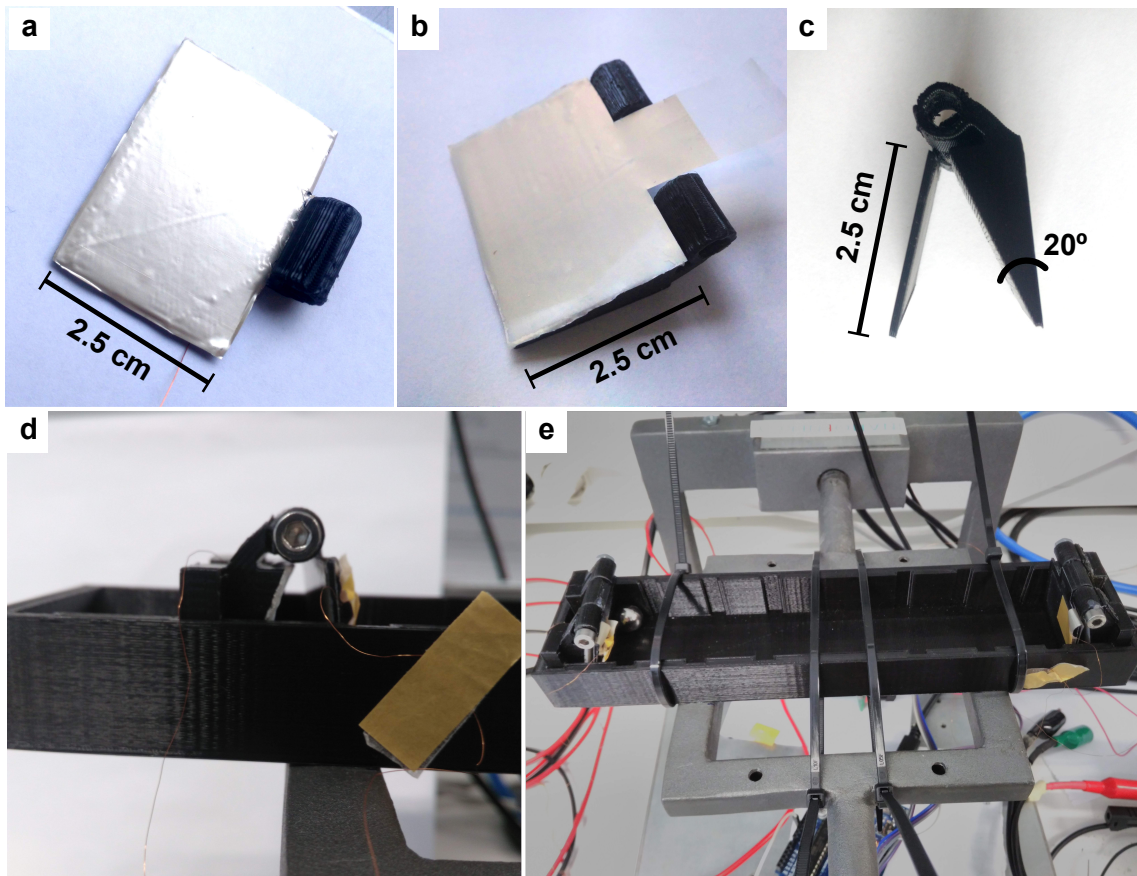


FIGURE 5.2: Photographs of the a) mobile part of the generator with Nylon/Ag; b) static part with PTFE/Ag; c) assembled generator with mobile and static parts; d) mounted generator on the modified track; e) the complete UL-TENG fixed to the rotative frame.

Due to the difficulty of soldering on silver, the connection wires were soldered on copper conductive tape adhered to a designed region of the silver layer carefully folded

to the back of each generator, so that the terminals were safe from any impacts (see in Fig. 5.2.a the wire leaving from the back and in Fig. 5.2.b the central extension of the PTFE/Ag layers to fold and create the contact terminal on the back). We used thin enamelled copper wires to eliminate any elastic force on the mobile part, then shielded cables for the high impedance measurements in section 5.5.

5.1.1 Typical electrical output

The two generators that compose the UL-TENG have the same working mechanism, represented in Fig. 5.3. The triboelectric layers of Nylon and PTFE are initially charged by contact electrification, due to the impact of the spheres that press the layers together. After the output stabilizes, we can perform measurements for different resistances connecting the electrodes. When the load is small, the peaks of current and voltage are similar to the one represented in Fig. 5.3.a. At first, the generator is at a resting position, and despite existing induced charges on the electrodes, there is no current being detected (i). When the Nylon layer approaches the PTFE layer due to the impact of the sphere on the mobile part, the electric potential distribution in space is modified, and since the load between the electrodes is very small, current flows freely to account for that modification (ii). With the generator fully closed, the electrostatic equilibrium is attained, there are no induced charges and the current is zero (iii). Finally, the opening of the generator imposes the flow of charges on the other direction (iv). During the separation, the current (speed of charge transfer) increases until reaching the positive peak, then decreases back to zero as the generator reaches the initial position, restoring the induced charges to their initial value (i). On the other hand, when the load connecting the terminals is very large, and the generator is at near open circuit (see Fig. 5.3.b), only a negligible current will flow through the load. Therefore, the induced charges barely change over the contact/separating cycle. When the surfaces are contacted (iii), no screening can occur, and the maximum measured potential is achieved. The separation motion of the layers restores the voltage to its initial value of zero, although a small peak can still be detected, when one is near but not exactly at the open circuit condition.

Note that the sphere impact does not produce a neat, clear peak as the models predicted, because the collision produces a much more complex motion of the layers than a sinusoidal compression. In Fig. 5.3.b are shown several small peaks from secondary impacts of the sphere, and/or the shaking of the mobile layer when it suffers a strong sphere

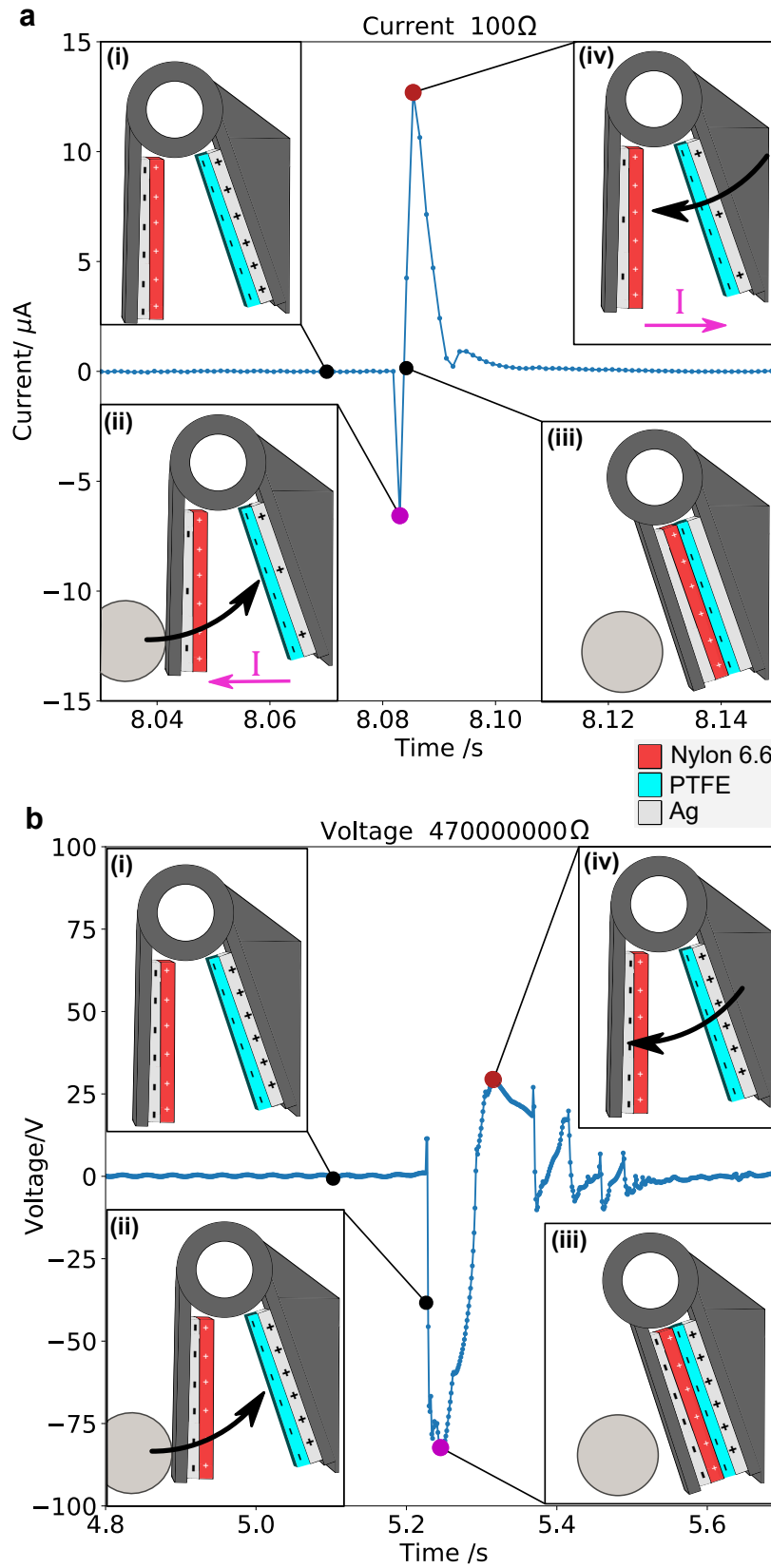


FIGURE 5.3: Working mechanism of each generator that compose the UL-TENG and their correspondence to a representative peak of a) short circuit current; b) open circuit voltage.

impact. In this work only the higher peaks were considered, because those small oscillations will be attenuated down to the noise level, making their acquisition more difficult, and they will not prejudice the output. On the contrary, they can only add to the energy transferred.

Another phenomenon observed was a significant attractive force between triboelectric layers. After the charging cycles, the electrostatic force of attraction between layers was great enough to keep the mobile and static parts together. When they were manually separated, they only glued again if brought into a proximity of 2 or 3 mm ($\approx 7^\circ$ between the two parts), suggesting the existence of a force that decreased in distance, such as the electrostatic force. However, both generators still kept their ability to be even more contacted when the sphere collided with the mobile part (since the output was preserved) or to open whenever there was a strong impact of a sphere on the opposite side of the track.

Nonetheless, this information can provide a valuable estimate of the electrostatic force. Each generator, even turned upside down, remains closed, therefore the electrostatic force must have an intensity at least equal to the weight of the mobile part, 20 mN (even considering the mobile part would not fall on the vertical, but with a rotation, the perpendicular gravitational force still is 99.3% of the total weight for 7°). Since the electrostatic force of attraction the plate 2 (for instance, Nylon) is subjected to is $F_2 = Q_2 E_1$, where Q_2 is the charge on plate 2, and E_1 is the field generated by the plate 1 (PTFE), then the absolute value of the force can be written as:

$$F_2 = \frac{Q_2 \sigma_1}{2\epsilon_0} = \frac{\sigma_S^2 A}{2\epsilon_0}, \quad (5.1)$$

where σ_1 is the surface charge density on PTFE, and symmetric charges on Nylon and PTFE are admitted for simplicity. This results on an estimated minimum value for the triboelectric charge density of $\sigma_S \geq 18.78 \mu\text{C} / \text{m}^2$, a value in the order of magnitude of the presented in the quantitative triboelectric series in section 2.1.

5.2 Optimizing the connection of TENGs

After the assembly of the two generators on the track arised the question of how to connect them to maximize the delivered power. Although parallel seemed the natural option, from a theoretical point of view, it should not be the best option. When one generator is

closed by the sphere impact, the track is tilted so that the other generator is at a higher position, and the tendency of the mobile part to continue to lie vertically means that generator opens, even if slightly, as the static part is tilted away from the mobile part. This way, the two generators are always in phase opposition, although the time duration of each voltage peak might not coincide. Consequently, when the output peak of a generator is positive, the other will be negative, so that connecting the TENGs in an antiparallel configuration would add the currents, reinforcing the signal. Therefore, the open circuit voltage V_{OC} and short circuit current I_{SC} of one generator and for four types of connections, parallel, antiparallel, series and inverted series were measured, summarized on Table 5.1 and compared on the graph Fig. 5.4. This study was conducted for track length L of 20 cm, period T of 2 s and A of 15° , and measuring time of each test of 120 s.

Configuration	$I_{SC} / \mu A$	V_{OC} / V
One side	6 ± 3	67 ± 24
Parallel	11 ± 2	95 ± 17
Parallel inverted	11 ± 3	97 ± 16
Series	6.0 ± 0.9	67 ± 24
Series inverted	2 ± 1	57 ± 10

TABLE 5.1: Study of different connections between TENGs for the construction of UL-TENG.

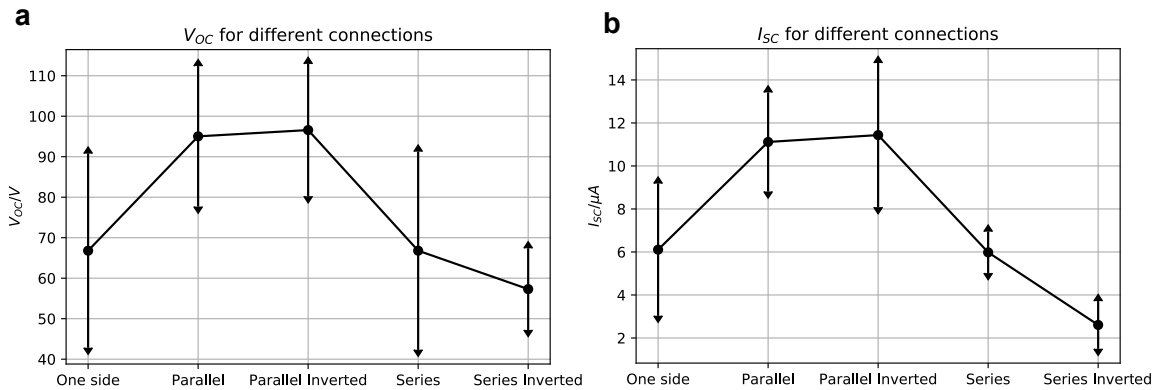


FIGURE 5.4: a) V_{OC} and b) I_{SC} measured for one generator and the 4 connection modes between the two generators that will compose the UL-TENG.

It is possible to observe that the parallel and antiparallel were the best connections, showing very similar results, but for the reason aforementioned and due to the slightly higher value of V_{OC} , the antiparallel configuration was chosen. In Fig. 5.5 is an example of a current measurement for both generators connected on the antiparallel configuration.

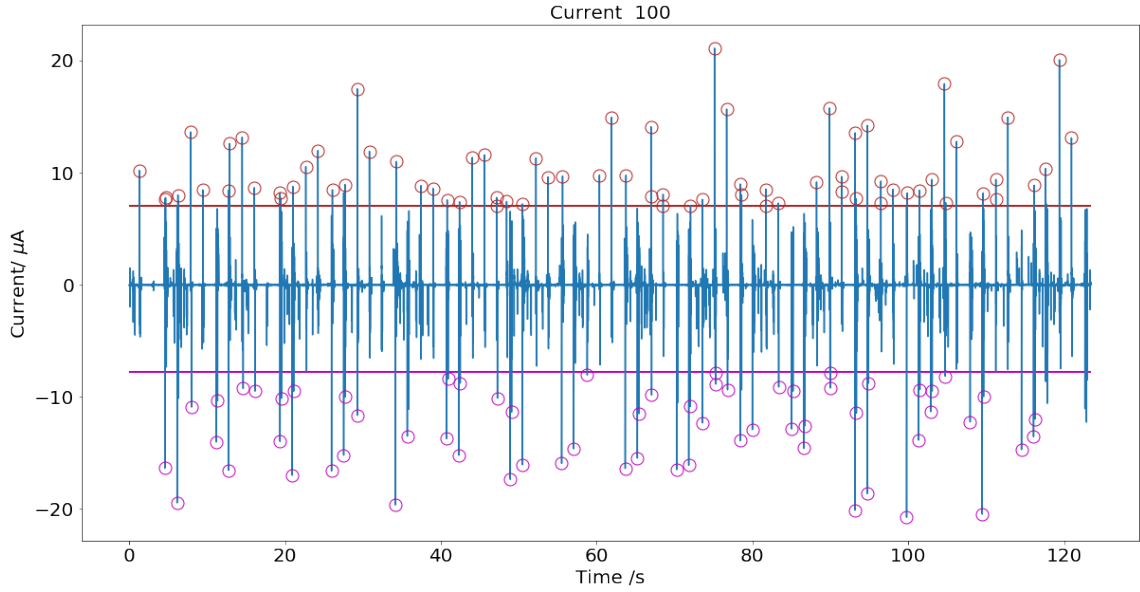


FIGURE 5.5: Sample of a current measurement at $100\ \Omega$ for the UL-TENG (both sides) for a period of 2s and pitch of 15° .

Later it was observed that the antiphase is more visible for the stronger sphere impacts, where the generator on the opposite end of the impact opens significantly, sometimes over 90° . In fact, stronger sphere impacts are directly associated with higher pitch values, that in turn maximize the separation between the triboelectric layers of the opening generator. This not only means the electrostatic attraction between layers is weaker, given more freedom of motion (rotation) to the mobile part of the opening generator, as the gravitational force takes a higher value, pulling on the mobile part along the direction of the track, helping it to open.

It is interesting that the inverted series connection showed electrical output even lower than a single TENG. In fact, in this configuration, the TENGs are competing against one another, in the sense that they are inducing a current in opposite directions on the same conductor.

5.3 Resistance characterization

Before starting the dynamical study itself, the optimum resistance needed to be determined, as shown in the resistance response graphs of Fig. 5.6. This was repeated for two extremities of the period and amplitude map: (1000 ms, 45°) and (3000 ms, 15°) (for 5° there was barely any output, as it will be explained further in this section). The resistances tested were $R \in [100, 1k, 10k, 100k, 470k, 1M, 4.7M, 10M, 68M, 100M, 470M]\Omega$.

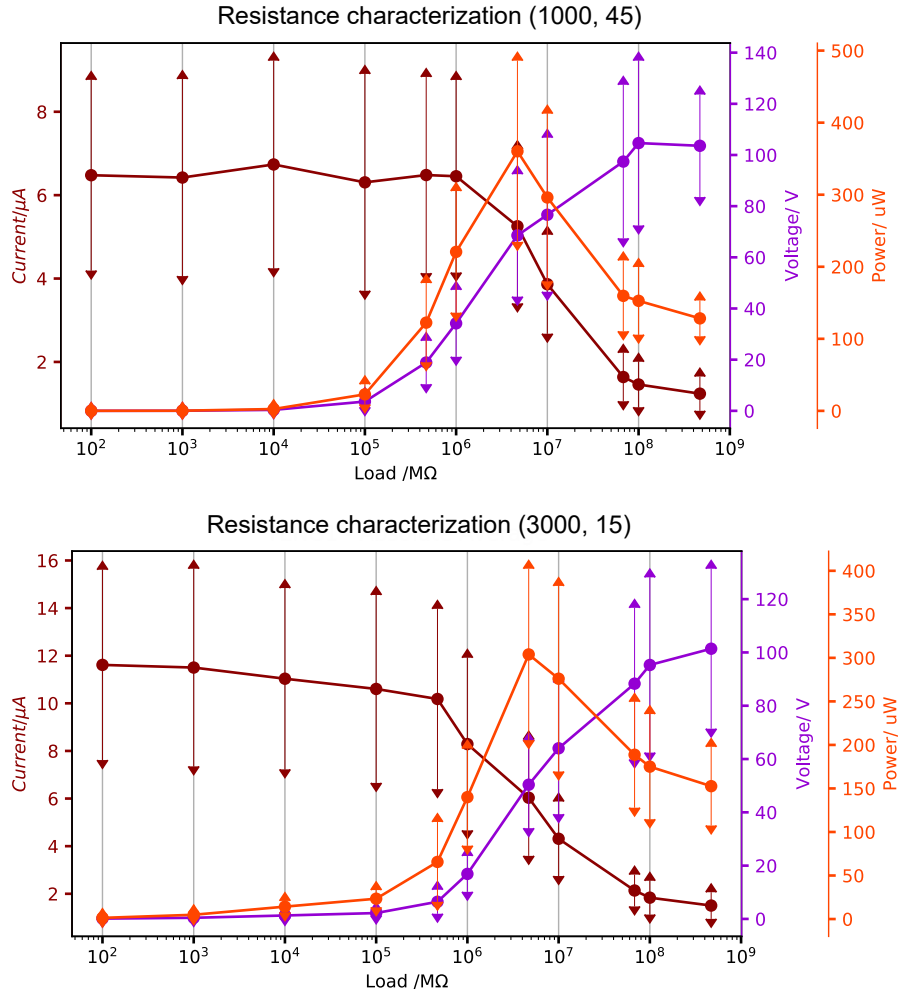


FIGURE 5.6: IPV curves for the UL-TENG at two operating pairs: (1000 ms, 45°) and (3000 ms, 15°).

Given the resistances used, we stress that the short circuit current is well determined, as opposed to the voltage for high impedance. Values of voltage at 470 MΩ were taken as near open circuit values. On the other hand, the maximum power is well defined, although limited to the resistor array resolution (see Fig. 5.6). We observe that the resistance of maximum power in both cases was 4.7 MΩ. Moreover, at high resistances, the current has not yet reached a very low value; this is a result of the difficulty of measuring low currents at high impedances without capturing external noise or having a leakage current that contributes to the overestimation of the measurement of current.

This value can be compared with the internal capacitance of the TENG. Although the capacitance varies with time during the operation of the nanogenerator, the total capacitance of the device was calculated from reactance measurements performed with an LCR (inductance, capacitance, resistance) meter for the closed (pressed and unpressed) and

opened (90°) configurations (see Fig. 5.7). Note that while capacitance is only dependent on the layers geometry and how far they are separated, the capacitive impedance depends on frequency, and that is the quantity that the LCR meter can measure. Therefore, the final capacitance for each configuration was considered the mean of all possible capacitance values calculated from the reactance measurements. The maximum, minimum and mean value of the capacitance for each configuration is summarized on table 5.2.

Configuration	Min C /pF	Max C /pF	$\bar{C} \pm \alpha$ /pF
Opened (90°)	3.89 ± 0.07	3.91 ± 0.07	3.90 ± 0.01
Closed (unpressed)	78.6 ± 0.2	78.7 ± 0.2	78.6 ± 0.1
Closed (pressed)	97.0 ± 0.2	97.9 ± 0.2	97.3 ± 0.2

TABLE 5.2: Statistical figures of the measurement of capacitance of the UL-TENG under different configurations.

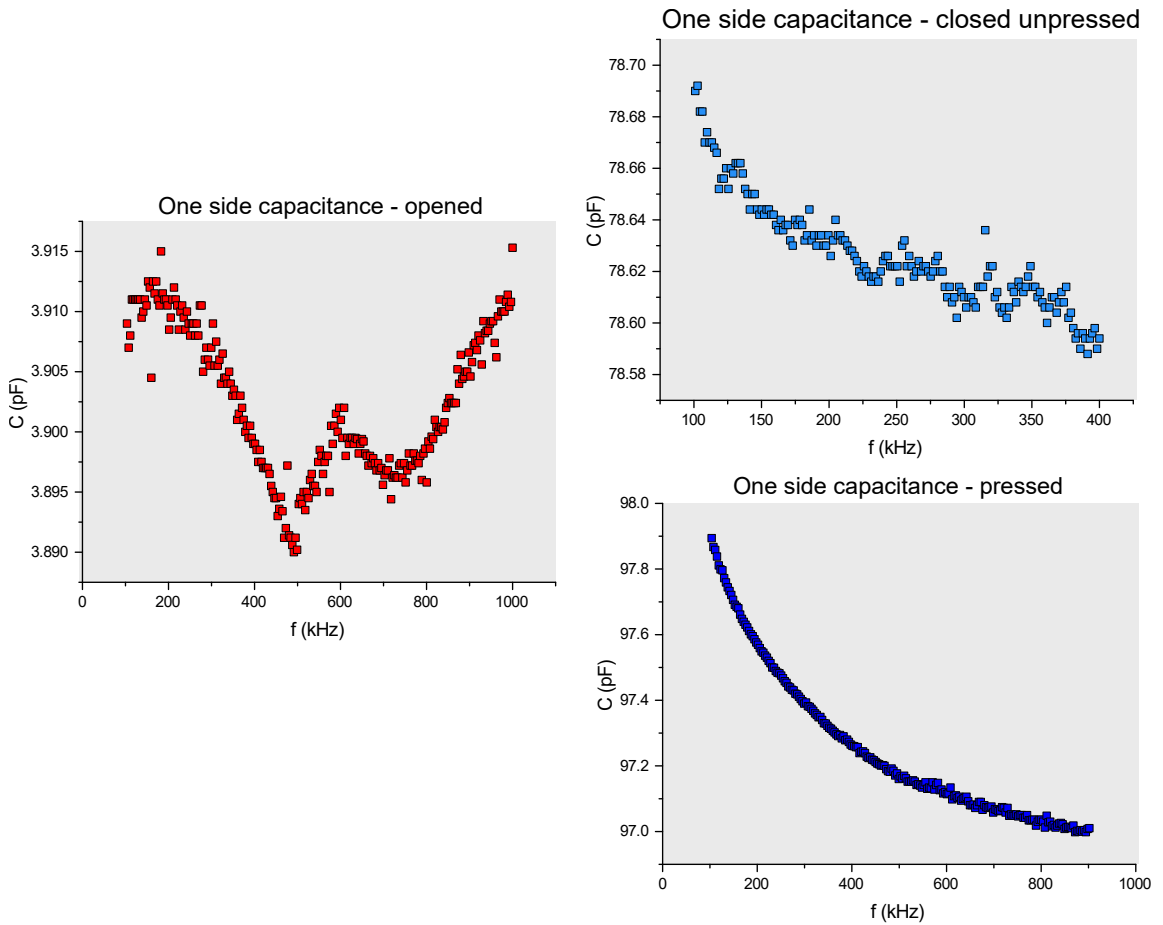


FIGURE 5.7: Graphs of the calculated capacitance of the UL-TENG under different configurations, from the measured reactance as function of frequency.

In fact, we can use these capacitance values to do a quick estimate of the optimum resistance order of magnitude with Eq. (2.29). Based on the time duration of the output peaks measured from the data files (10 - 20 ms), we calculated a range of angular frequencies; from the range of capacitances on table 5.2, we obtained optimum resistance values from 16.4 M Ω to 816 M Ω , being the first one correspondent to the pressed configuration and 10 ms of total peak width in time. Converting those values to the estimated parallel impedance of the UL-TENG, we arrive at a 8.2 M Ω - 408 M Ω . Since the capacitance of pressed and unpressed layers is within the same order of magnitude, and each nanogenerator spends more time on the closed configuration due to the electrostatic attraction, the value of 8.2 M Ω seems a good estimate of the optimum resistance of 4.7 M Ω as determined by the IPV curve.

5.4 Dynamical study of the UL-TENG

The UL-TENG can be distinguished by its capability of decoupling the time duration of closing/opening of the layers from the motion period: the period is dictated by the track and buoy motion, while the period of closing/opening depends on the final velocity of the rolling spheres, that accelerate along the track before reaching each end. As it has been hinted in the previous chapters, the focus of this study was to investigate the performance of the UL-TENG for different track lengths, periods and pitch amplitudes. This is the basis of the optimization of our device: understanding its behavior at different parameter combinations. The UL-TENG was purposed to power small electronics on a 1:8 scale navigational buoy, therefore the motion dynamics are not imposed by any spherical encapsulation, but rather depend on how the wave motion will affect the scaled buoy. The commercial buoy operates at a range of wave periods of 2.1 to 10 s, and wave heights of 0.5 to 2 m, that were converted by the Froude similitude law to periods from 0.742 to 3.536 s and heights from 6.25 to 25 cm, respectively [4]. The periods chosen were $T \in [1000, 1500, 2000, 2500, 3000]$ ms (1 s is the minimum period due to the servo motor torque limitations). On the other hand, the track lengths used were $L \in [5, 10, 15, 20]$ cm, values dictated by the size of each generator and the size of the 3D printer. Finally, the mentioned wave heights correspond to pitch rotations from 3° to 12.5° for a track length of 20 cm, and for a 5 cm track, to pitches between 12.5° and 50°. Therefore, the chosen values for pitch amplitudes were $A \in [5^\circ, 15^\circ, 25^\circ, 45^\circ]$.

During the course of this study, a sort of beatings on the output peaks were observed (see Fig. 5.8). These beatings can be either due to synchronization issues between the sphere motion and the ideal sphere motion for that track, or due to the acquisition itself. The first appointed cause was indeed observed for lower pitches and longer periods, where the sphere would be oscillating at the middle of the track, reach the end of the track after some seconds, collide with one or two generators for some cycles, then go back to oscillating at the center. The second reason is that the Electrometer sends data from 2.932 to 2.932 s to Labview, losing ≈ 340 ms of data in the process - each new batch of data is appended to the existent data on Labview. For periods of 3 s, for instance, these communication events could synchronize with the peaks, leading to long intervals of time with zero output, as represented on Fig. 5.8.a.

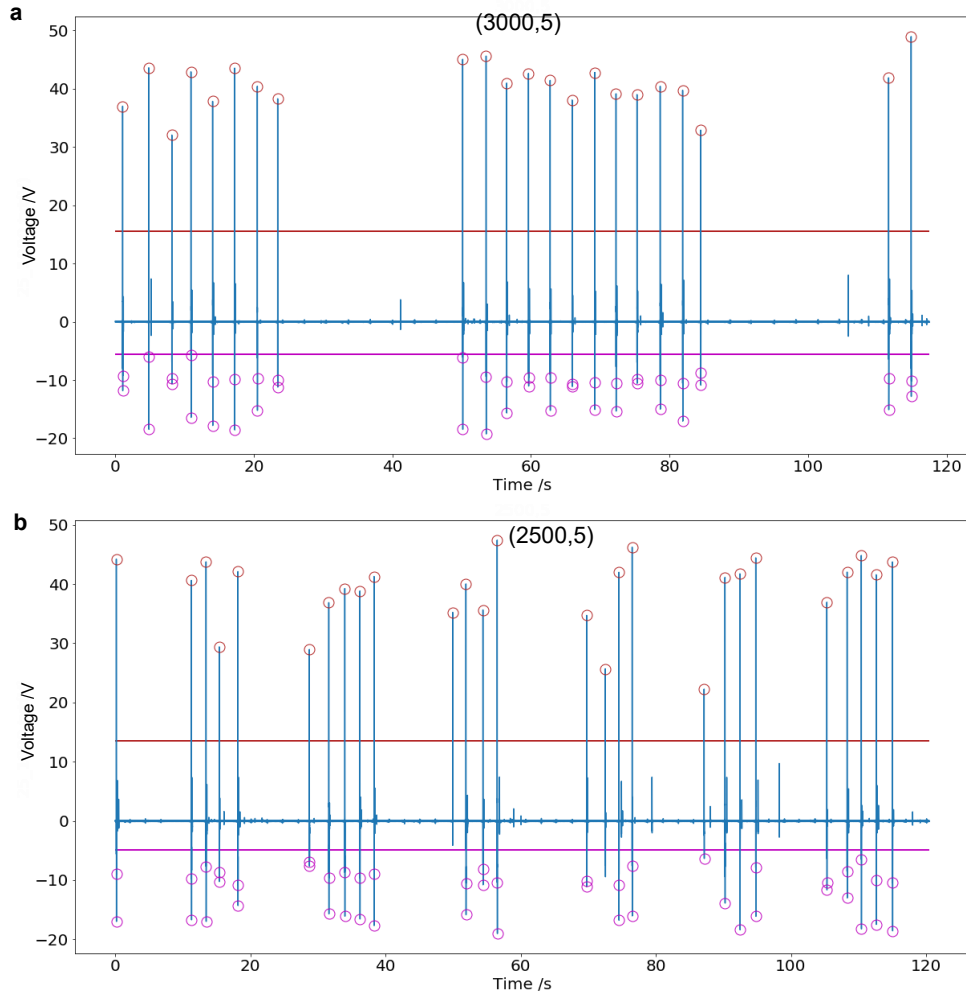


FIGURE 5.8: Examples of beats occurring at a 5 cm track length for a) (3000 ms, 5°); b) (2500 ms, 5°).

However, as long as we keep the acquisition time long enough (longer than the period

of the beating) and prevent the very low peaks to be included in the averages on the analysis software, the beat phenomena should not have an impact on the final output.

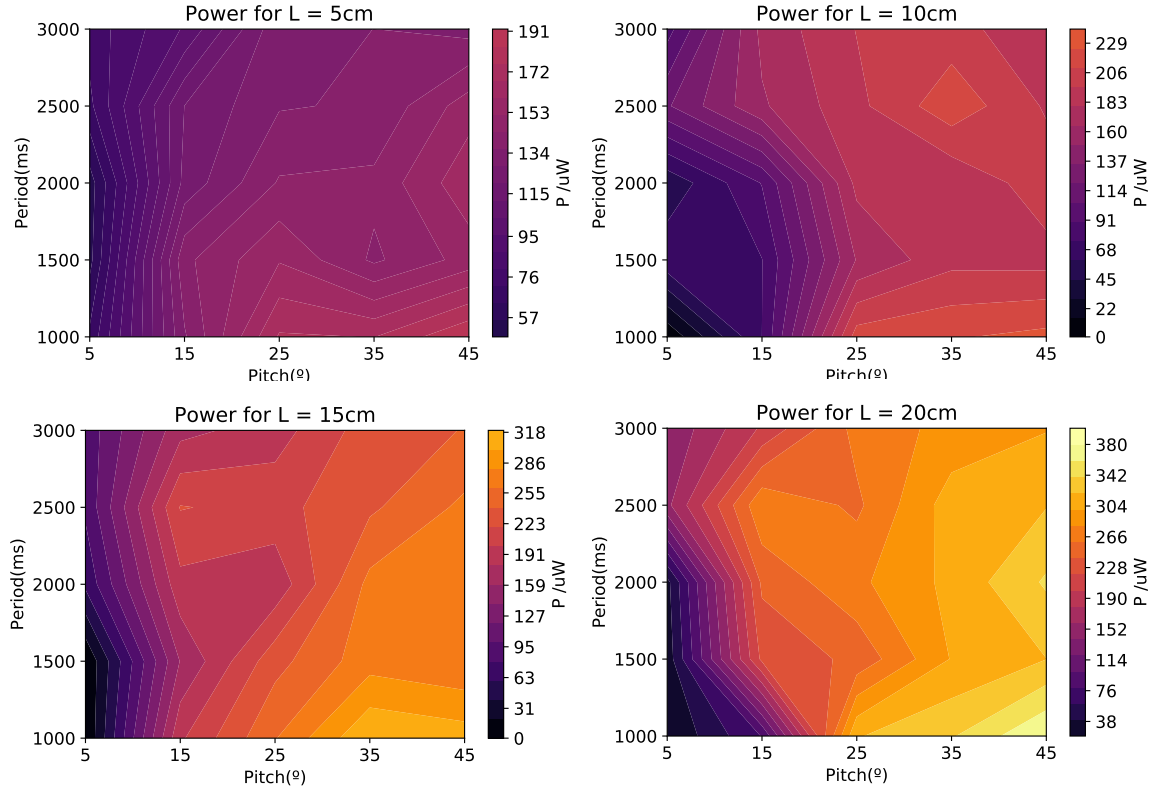


FIGURE 5.9: UL-TENG generated power for each track length (normalized colors to the maximum and minimum displayed values).

After being charged for over 1000 cycles, the current and voltage were measured for all the referred parameter values (L, T, A). The first observation we can make is that the maximum power increases with the track length. Moreover, the region of higher power is located towards the high pitch, low period corner until $L = 15$ cm [with the exception of the pair (2500 ms, 35°) for $L = 10$ cm]. For $L = 20$ cm, this region spreads slightly to higher periods. This can be related to the fact that more time is needed for the sphere to reach the end of a longer track, therefore the optimal periods increase with L . On the other hand, pitch is the determinant parameter on the power output, since the gradient of increasing power is predominantly along the pitch direction. As for small pitches at the bottom left corner, they are better harvested for the 5 cm track length, since the period and amplitudes are too small for the sphere to reach the end of the longer tracks.

Due to these variations of the region of higher power, we found it interesting to investigate if there was a best L for each pair (T, A). It appears the 20 cm track is the more suitable to harvest the most part of the (T, A) map (see Fig. 5.10), but in fact, in Chapter 6

this prevalence of the 20 cm track will be better understood. As for the rest of the map, it agrees with the explained before, the ability of smaller tracks to harvest smaller periods and pitches, as well as the optimum periods increasing with the track length.

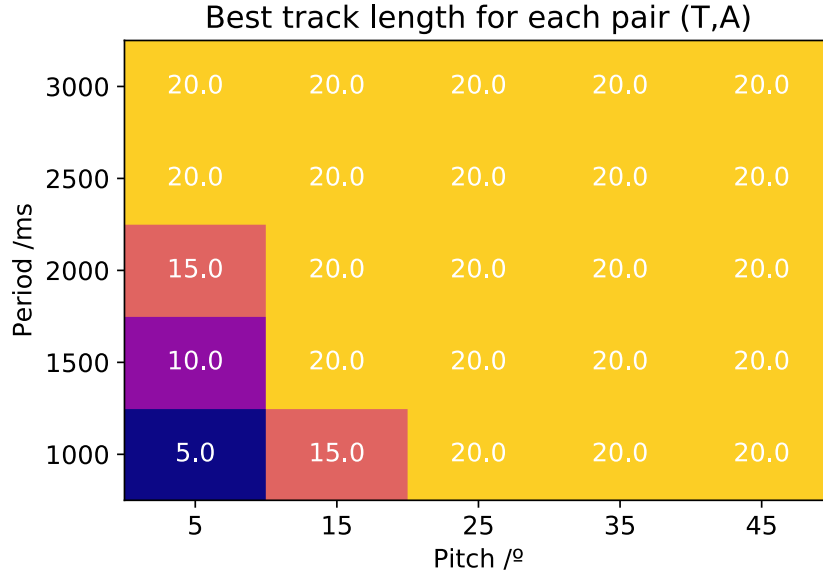


FIGURE 5.10: Best track length (L), in cm, for each pair of period and amplitude.

5.4.1 Coupled UL-TENG and comparison

Following the discussion on the connection methods arised the question if the two generators could be more synchronized, so that the effect of adding constructively the output peaks of each generator would be more pronounced. The solution was to couple the two generators with a non extensible thread, creating the coupled UL-TENG. This way, when the sphere closed one generator, it opened the other automatically until the angle between the surfaces was 40° (the double of the angle at resting position). The track length study was reproduced for the same parameters as in the last section, excepting for the 5 cm track, since there was the risk of collision between the two mobile parts, due to always being open for a certain angular amplitude. In Fig. 5.11 are the power maps for 10, 15 and 20 cm.

Similarly to the previous study, the maximum power increases with the track length; however, while in the uncoupled UL-TENG the maximum power obtained was $380 \mu\text{W}$, for 20 cm, that value is only at mid range for the coupled UL-TENG and all the tested tracks.

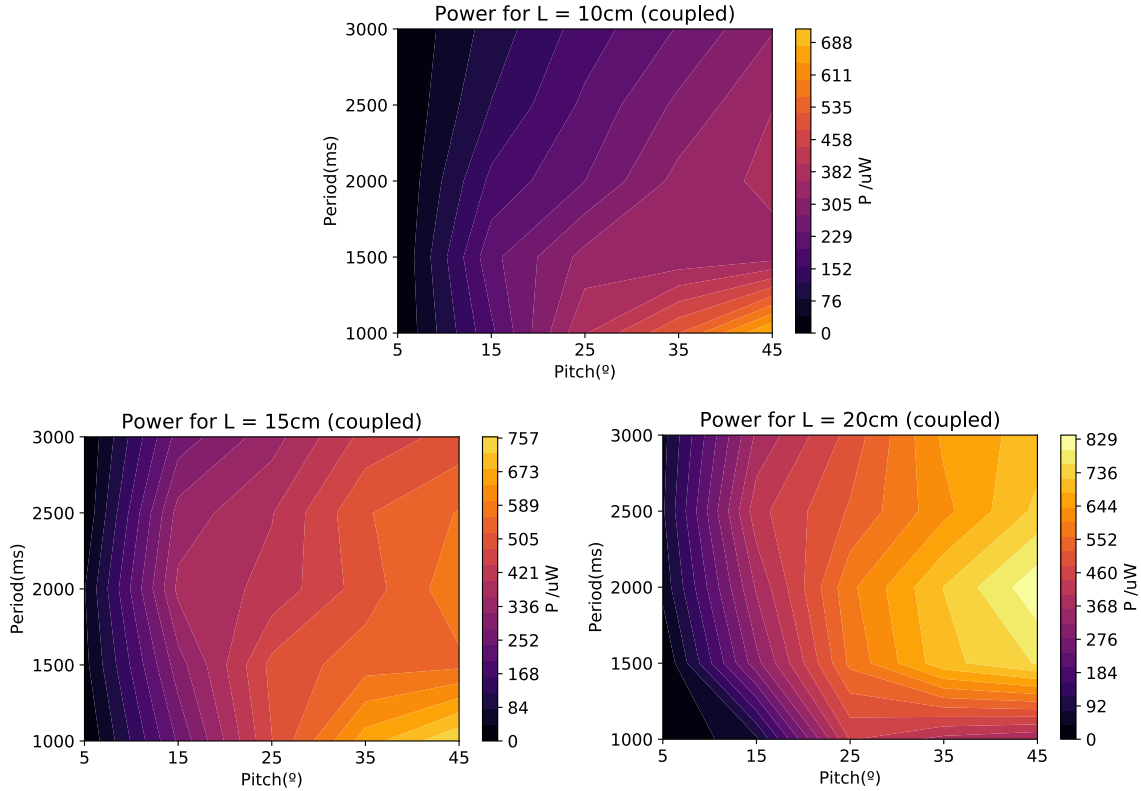
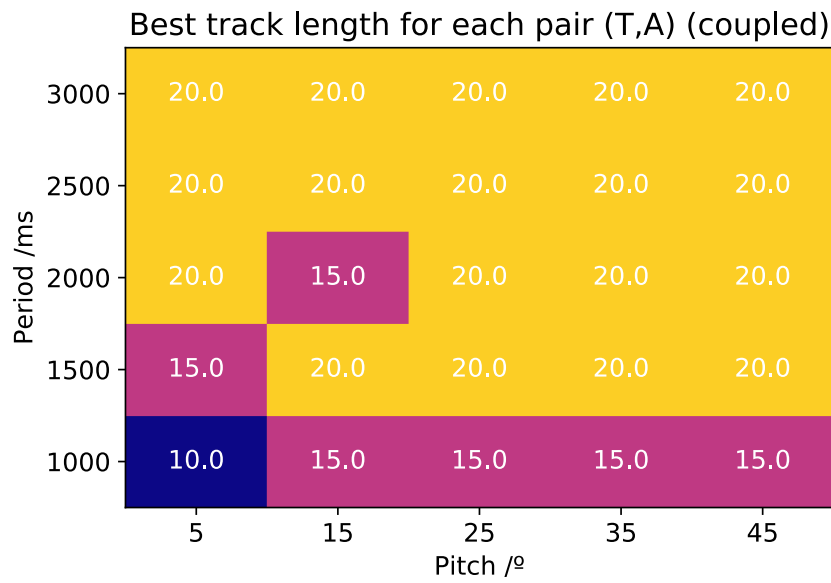


FIGURE 5.11: Power generated by the coupled UL-TENG for each track length (normalized colors to the maximum and minimum displayed values).

Additionally, the region of higher power is more well-defined than in the previous study, and as track length increases, it also moves towards longer periods. The best L for each (T, A) for the coupled UL-TENG is represented in Fig. 5.12. It shows some differences, mainly because of the narrow high power region for 20 cm, causing the track of 15 cm to be the best for all the pitches with period of 1000 ms.

In order to better visualize the evolution of power with track length and the differences between the coupled and uncoupled UL-TENG, the graph of the maximum power for each track length was created (Fig. 5.13). Although a reduced number of track lengths were tested, the maximum power seems to increase linearly with the track length, as supported by the fitting parameters in Table 5.3. The coupling seems to be an intrinsic effect as expected, since the coupled UL-TENG consistently has a higher output relatively to the uncoupled version, for all track lengths, although the two slopes are very similar. The UL-TENG was capable of generating a power of $381 \pm 241 \mu\text{W}$ (equivalent to a power density of 1.9 Wm^{-3}) and its coupled version $829 \pm 365 \mu\text{W}$ (equivalent to a power density of 4.1 Wm^{-3}), at the longer track tested. Nevertheless, note the relatively high standard deviations, illustrating the need for measuring current and voltage for a larger period of

FIGURE 5.12: Best track length of the coupled UL-TENG, for each (T, A) .

time, and consequently allowing the selection of a smaller and more meaningful region of values around each mean value.

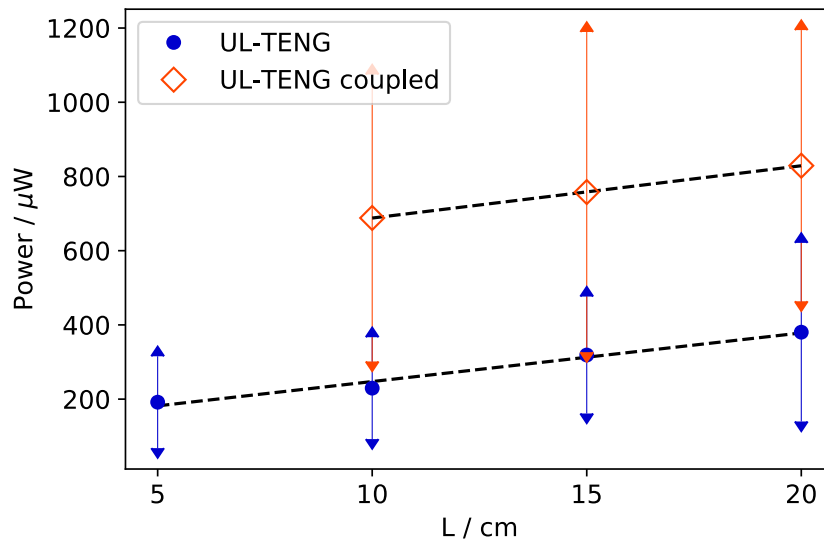


FIGURE 5.13: Comparison of the maximum power, for each track length, between the coupled and uncoupled UL-TENG.

Equation	Device	$m \pm \Delta m$ ($\mu\text{W}/\text{cm}$)	$\frac{\Delta m}{m}$ (%)	$b \pm \Delta b$ (μW)	$\frac{\Delta b}{b}$ (%)	R^2
$P_{max} = mL + b$	UL-TENG	13 ± 1	10%	116 ± 18	16%	0.98
$P_{max} = mL + b$	UL-TENG coupled	14.09 ± 0.07	0.5%	547 ± 1	0.2 %	0.99997

TABLE 5.3: Fitting parameters of the maximum power dependence on track length for coupled and uncoupled UL-TENG.

5.4.2 Effect on the optimum resistance

After the track length studies were performed, we set to enquire whether the dynamical parameters of (T, A) affected the optimum resistance, but it had not been detected due to the large range, low resolution group of resistances available on the resistances box used. Therefore, a set of 6 resistances only in the range of 1-10 $\text{M}\Omega$ were chosen to have the electrical output of the coupled UL-TENG manually measured: [1, 2.19, 3.97, 5.76, 7.4, 9.95] $\text{M}\Omega$. The tests were conducted for the pairs (1000 ms, 45°) and (3000 ms, 15°), similarly to what was done in section 5.3, and the corresponding IPV curves are presented on Fig. 5.14.

While in section 5.3 there was no detectable difference between the two sets of period and amplitude, with better resolution on the resistance, we observe that the optimum resistance for (1000 ms, 45°) is 3.97 $\text{M}\Omega$, while for (1000 ms, 45°) is 7.4 $\text{M}\Omega$. However, in the previous automated studies, carried out with the resolution the resistances box provided, the best resistance at the date was in fact 4.7 $\text{M}\Omega$.

This result leaves an open question: what can be changing between these two pairs of (T, A) to provoke such a change in optimum resistance? Recalling Eq. (2.30), this could be related to the velocity of the layers approximation. Still, how is this behavior related to the motion parameters (T, A) ? Later, in Chapter 6, these results will be better understood and these questions answered in detail.

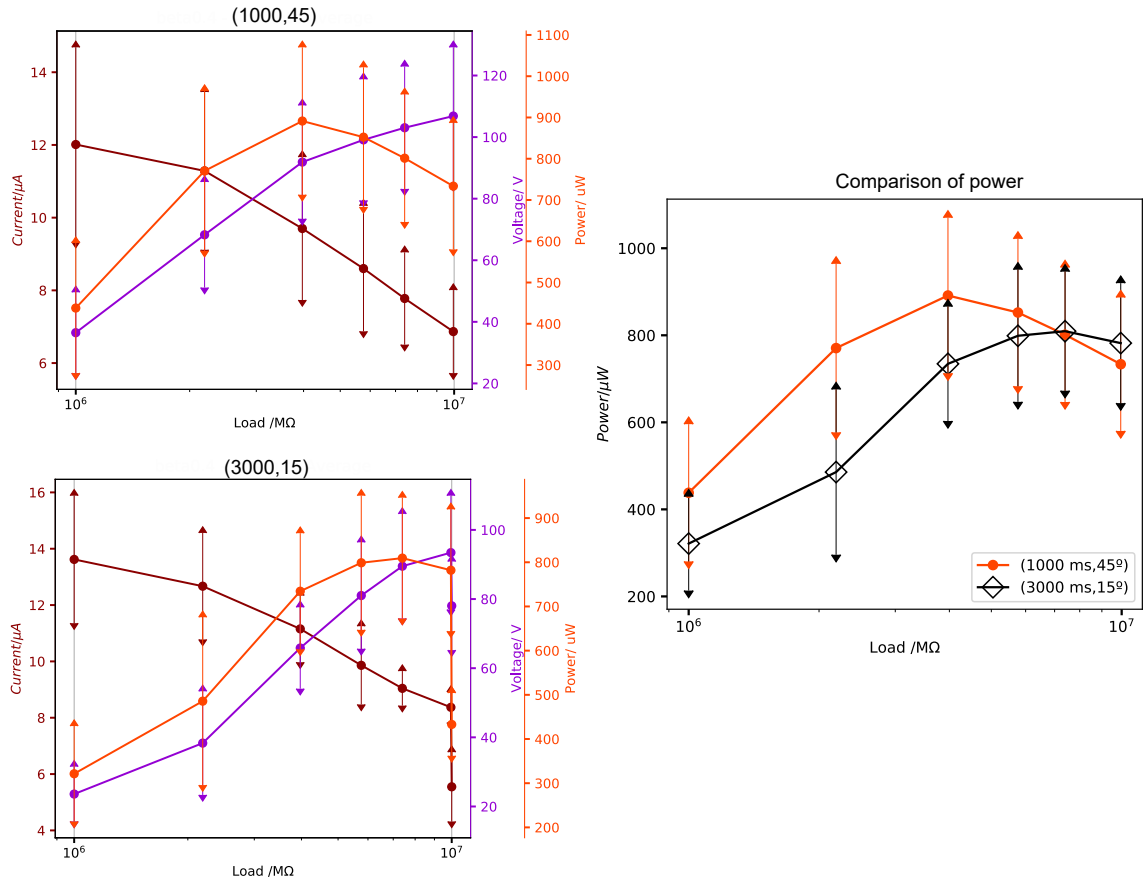


FIGURE 5.14: IPV curves of the UL-TENG for different dynamical conditions, for resistances between 1-10 MΩ.

5.5 Charging effect of the spheres

The last route explored to optimize the UL-TENG was increasing the surface charge density. It is true that the UL-TENG, being a single area TENG, always has the same area of contact, despite how the collision of the spheres. However, promoting a better contact between layers by pressing them with a higher force could enable charge transfer on portions of the insulators where it did not occur before. In our device, this can be accomplished in a simple way, by increasing the number of spheres that roll and collide with the mobile part of each generator. To explore this questions the open circuit voltage and the short circuit current of one generator at (1000 ms, 45°) was measured. To understand if the charging effect was the answer, some specific steps were taken at the procedure and electrical level.

At first glance, more spheres will have a stronger impact force and can transfer more momentum to the mobile part of each generator, besides the charging effect. Therefore, the TENG was charged with 1 to 4 spheres for over 1000 s and always measured with 1

sphere for 120 s. To avoid residual charges to affect the results in between trials, the triboelectric layers were discharged after each test, and the order of the spheres randomized. Discharging the layers consisted in cleaning both with acetone and alcohol, so that any pieces of material could be removed, and the humidity in those solutions could capture the excess of charges trapped in the surfaces of the insulators. The discharging was confirmed by the disappearance of the electrostatic attraction after cleaning and the charging behavior the TENG showed afterwards. However, while they separated well if only PTFE was discharged, if the same was done for only Nylon, the layers would continue to be attracted and the output was unchanged - which may indicate that Nylon is not an easy insulator to discharge (and charge) comparatively to PTFE.

Since we needed to get the closest possible to open circuit voltage, we used a resistance divisor with two resistances of 5 G Ω . Next, to reduce errors and leakages, the enamelled copper wires were replaced by shielded, well isolated cables and the PCB commutator was not included. Firstly, because the main purpose of the PCB is to serve the automated measurements with the Box of Resistances, which was not used here; but above all, because it would defeat the purpose of using the shielded cables. The Electrometer terminals on this PCB are very close and unprotected, so that it is possible, for high impedance measurements, that leaks occur through the PCB material. This fact should be taken into account on a future design of the PCB and/or future measurements of open circuit voltage.

We observe that V_{OC} always increases with the number of spheres used in charging, for the numbers tested. Recalling its equation as provided by the capacitive model, $V_{OC} = \frac{\sigma_S z}{\epsilon_0}$ [see Eq. (2.23b)], this behavior could be attributed to an increasing surface charge density. Note that the open circuit voltage (see Fig. 5.15) for the TENG charged with 1 sphere is close in value [slightly higher since this test was done in a better (T,A)] to the “one side” on the connection study, showed in Fig. 5.4.

The short circuit current has a very similar response to the number of spheres used in charging, although trending towards a constant value. Looking back to Eq. (2.20), $I_{SC} \propto \sigma_S$, just as the open circuit voltage. Hence, the number of spheres seems to in fact promote more efficient contact between insulators, therefore increasing the surface charge density. However, this behaviour should saturate for a certain number of spheres, above which the contact would not be improved significantly. This way, and to minimize the degradation the impact of a great number of spheres provokes, the UL-TENG could be

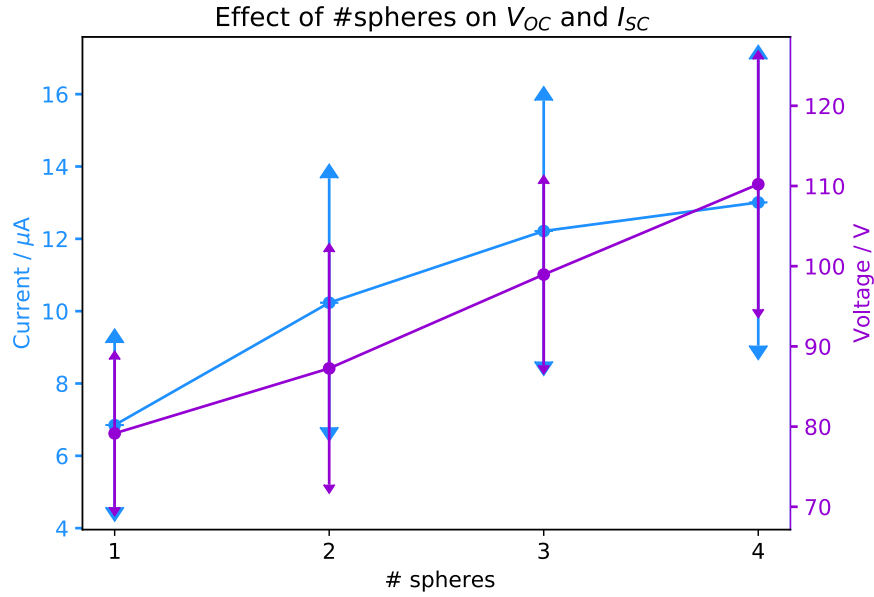


FIGURE 5.15: V_{OC} and I_{SC} for one generator, when charged with 1, 2, 3 or 4 spheres.

pre-charged with spheres or other mechanism to assure a good contact, and then used with only one sphere.

5.6 Storing energy from the UL-TENG

When the output of a TENG is rectified, it can be used to charge different capacitors to power other small electronic devices. The rectifying circuits we used were half wave, full wave and Bennet's Doubler (see Fig. 5.17). Different charging efficiencies can be obtained with different capacitor values (according to its matching to the capacitance of the TENG) but also with different periods of closing/opening the TENG. We chose the best pair for the track length of 20 cm (1000 ms, 45°), with only one sphere, and were able to charge a 10 nF capacitor to 112, 121 and 83.9 V in 1 min and 30 s, with the full wave rectifier, half wave rectifier and Bennet's Doubler circuit, respectively. This corresponds to stored energies between 35 and 73 μJ . Note that the discrete steps resulting in a voltage increase at each sphere impact on the UL-TENG are visible in Fig. 5.16.a. Nonetheless, also visible is some self discharge on the half and full wave configurations.

The Bennet's Doubler is a rectifying circuit that possesses, as opposed to the half wave and full wave circuits, two capacitors: one of smaller capacitance C_{store} , to store small quantities of charge, to be delivered periodically at a larger capacitance C_{res} , the reservoir.

The main advantage of this circuit is that the voltage in C_{res} never reaches the saturation phase as the other two rectifiers [105], and, with enough time, surpasses their saturation voltages. However, the charge accumulation in C_{res} is slower than in the other two circuits. With this circuit, the coupled UL-TENG with 4 spheres was put to test. To better mimic real applications of such device, for instance a wireless communication device, a resistor R_L of $9.95 \text{ M}\Omega$ was added to the Bennet's Doubler configuration, connected to C_{res} (see Fig. 5.17). New values of capacitance were tested, and the UL-TENG at its maximum capacity was able to charge a $10 \text{ }\mu\text{F}$ capacitor to 1.71 V and a $68 \text{ }\mu\text{F}$ to 0.625 V in 4 min and 30 s, corresponding to a stored energy of 14.6 and $13.3 \text{ }\mu\text{J}$, respectively. Note that the values of the capacitors C_{store} and C_{res} were not optimized for the UL-TENG. Still, the UL-TENG is already halfway through reaching a stable level of 3.3 V (for a capacitor of $10 \text{ }\mu\text{F}$), and starting to feed low power electronics.

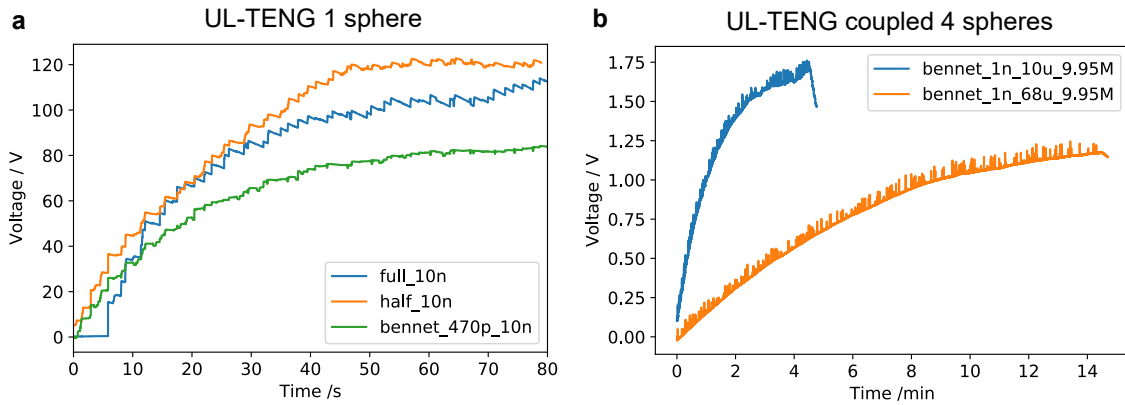


FIGURE 5.16: a) Charging curves of the full, half and Bennet's Doubler configurations for $C_{res} = 10 \text{ nF}$ and $C_{store} = 470 \text{ pF}$, for the UL-TENG operating with one sphere. b) Charging curves of the Bennet's Doubler configuration for $C_{res} = 1 \text{ nF}$ and $C_{store} = 10 \text{ }\mu\text{F}$ and $C_{store} = 68 \text{ }\mu\text{F}$, for the coupled UL-TENG charged and operating with four spheres.

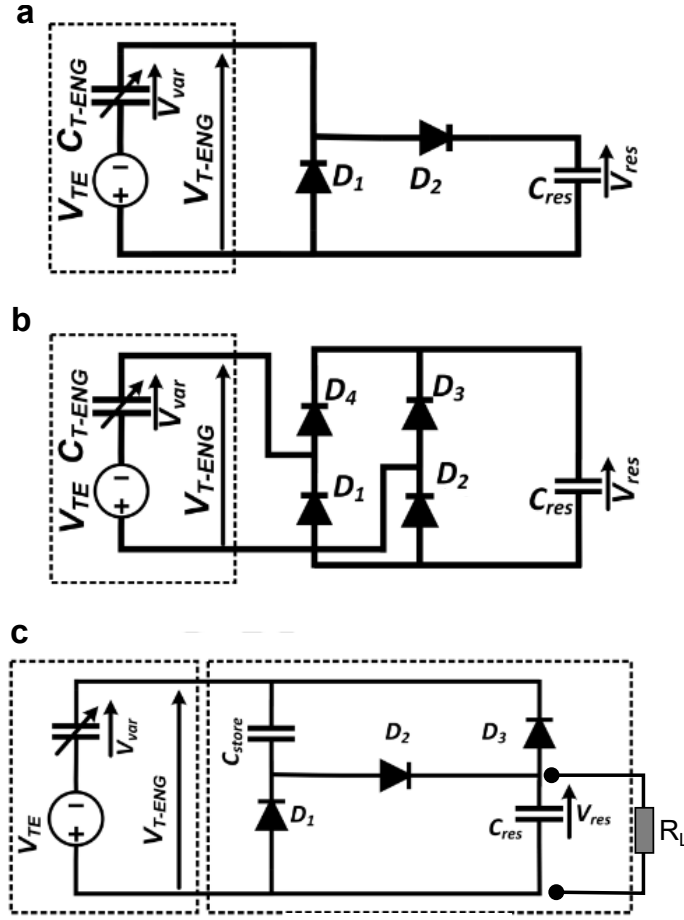


FIGURE 5.17: Rectifying circuits used in this work: a) half wave; b) full wave; c) Bennet's Doubler, with a resistive load connected to the terminals of the reservoir capacitor C_{res} . The TENG equivalent circuit is represented on the left for all circuits. Adapted from [105].

5.7 Summary

From the current and voltage measurements of the UL-TENG, it was possible to understand its working mechanism in depth and take advantage of the antiphase motion of the generators, connecting them in an inverted parallel configuration. The determined optimum resistance of $4.7 \text{ M}\Omega$ of the device was later found to vary with the dynamical pair (T, A) , possibly related to the velocity of the layers motion, as it will be discussed in Chapter 6.

The multiparametric study on track length, period of motion and pitch amplitude showed a consistent increase of power of the UL-TENG with track length, both for the regular and the coupled version of the device. The coupled UL-TENG showed a 2-fold

increase in maximum power density, due to the synchronization of the positive and negative peaks through the antiparallel connection. However, the coupled version showed a more narrow region of high power. This region might be related to a faster sphere, with a stronger impact on the UL-TENG. Nonetheless, more information will be provided on this topic on Chapter 6. While the best pitch is always the maximum, that might not be the case for period, since longer tracks harvest longer periods better. To account for this information, a map of the best track length for each pair of (T, A) was built to provide future guidance on the design of new TENGs.

Incorporating more spheres into the UL-TENG showed that pressing the layers together with more force of impact and/or helping the mobile layers to contact more evenly on the static part increases the saturation charge of the triboelectric layers. Since the use of more spheres will incur on higher degradation, determining if there is a best number of spheres to maximize the output of the device from this perspective will allow to pre-charge of the layers, while keeping its normal functioning with one sphere.

Chapter 6

Multiphysics modelling and simulation of dynamical and electrical performance

To better understand how the dynamics of the track motion of the UL-TENG affects the electrical output, three different simulations were performed: a numerical simulation of the motion profile of a sphere on a rotating track mimicking the UL-TENG; a numerical simulation on the power generated by such moving sphere, employing both the CA model and the finite element method with COMSOL Multiphysics®; and finally a simulation of the generated energy for a fixed time interval.

The first objective was to investigate the role of the parameters that rule the dynamics of the UL-TENG in the sphere motion, namely their influence on the i) whether the sphere reaches the ends of the track; ii) the sphere final velocity when reaching the mobile part of the TENG; the possible existence of iii) impact velocity gradients and (iv) optimal optimal operating points in the (T, A) space.

These dynamical parameters are the same that are given to the experimental 1-axis of rotation system to simulate the wave motion. They are the period of oscillation (T) and the maximum pitch for that test, (A ; rotational, angular amplitude).

Simultaneously, a thorough relationship between the approaching velocity of the triboelectric surfaces and generated electrical power also needs to be established, linking the parameters (T, A) to the electrical output. Thus, it was assessed if and how velocity

affects the open circuit voltage and short circuit values; the optimum resistance and the maximum power value.

Finally, a strategy to assess the impact of the parameters (T, A) on the energy transferred (at optimum impedance) was developed, on the assumption that low power peaks with a high frequency could surpass higher power peaks with lower frequency, that is, generating more energy. This would make the periodicity of impacts T a variable to consider when optimizing a device, besides the maximization of power.

All these simulations are not independent, but rather interconnected: the sphere motion simulation predicts a set of impact velocities, that are converted to the initial closing velocities of the TENG. Moreover, to calculate the energy generated, both the closing velocities of the TENG and the correspondent power need to be calculated beforehand. Thus, this chapter is a product of a continuous and progressive effort towards a each time more complete description (and prediction) of the performance of the UL-TENG.

A crucial connection between the different simulations is the collision of the sphere with the mobile part of the generator, as represented in Fig. 6.1. Note that the angle between the static and mobile parts of the TENG represented in the figure is exaggerated; in reality, it is a very small angle ($\approx 5^\circ - 7^\circ$), so that approximations can be performed as will be verified later in this chapter. In particular, this implies that approximately all momentum lies on the x-axis. Although it is true that for some (T, A) combination small oscillations, are experimentally observed after the first impact of the sphere, in the simulation case, the collision mechanism needs to be simplified. Therefore, we assume that all of the sphere momentum is transferred to the mobile part of the generator, “gluing” the sphere to it after the collision, in a perfectly inelastic collision. In fact, this is always the best case scenario, as it transfers the maximum velocity possible from the sphere to the mobile part of the TENG. That velocity conversion derives from the conservation of momentum (along one axis), according to the masses of the sphere and the mobile part of the TENG:

$$v_i = \frac{m_{\text{sphere}}}{m_{\text{mobile}}} v_f, \quad (6.1)$$

where v_f is the impact velocity, or final velocity, of the sphere, and v_i is the closing velocity of the mobile part.

Another important remark is that, as discussed in Chapter 5, each nanogenerator of

the UL-TENG has a waiting time between the close/open cycle. However, we are simulating repeated cycles to improve the efficiency of the simulation, because if any waiting time was considered ($\sim$ seconds), temporal resolution would be wasted on a null electrical output. Nonetheless, since in this section we are interested in the generated electric power, this will not influence the obtained conclusions. It will only become important when discussing the simulated energy.

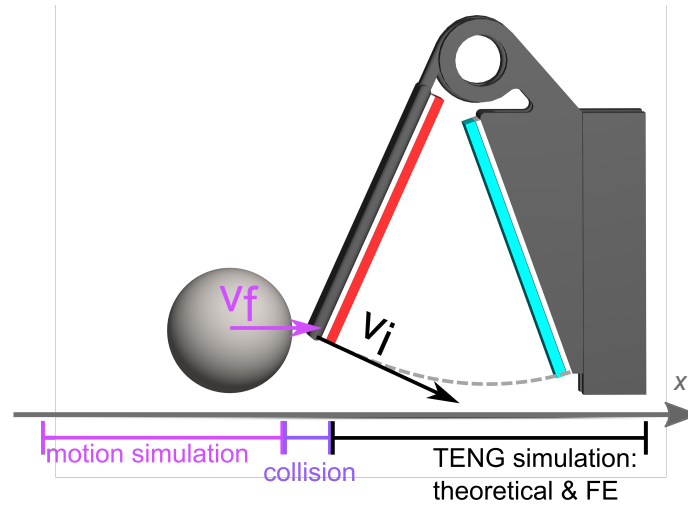


FIGURE 6.1: Schematic of the different moments of the UL-TENG operation and corresponding simulations.

The modelling of the UL-TENG was made possible by an iterative process of tweaking and improving each simulation with observations from the other and, of course, after experimental observations of the generator behavior. The material parameters used were also consistent with the assembled generator, except for the triboelectric surface charge, that was chosen within a reasonable range but was not directly measured. These parameters are shown on Table 6.1, and were kept constant for all simulations. For all these reasons, within the limitations of the simulation methods, the UL-TENG is simulated as consistent as possible.

Parameter	Value	Parameter	Value
L	2.5 cm	W	4 cm
Area	10 cm ²	σ_s	50 $\mu\text{C} / \text{m}^2$
ϵ_{r1}	2.75	ϵ_{r2}	4
d_1	50 μm	d_2	17 μm

TABLE 6.1: Simulation parameters of the UL-TENG electrical characteristics for several closing velocities. Dielectric 1 corresponds to PTFE and dielectric 2 is Nylon.

6.1 Simulation of one dimensional sphere motion

A detailed description of the UL-TENG must rely on the basic understanding of the sphere motion on the moving track. As different behaviors were being observed on the experimental setup, this rather simple model was being created and constantly confronted with those observations. The model starts assuming the sphere moves only in one dimension, along the length of the track, and that it rolls without slipping (assumptions based on experimental trials). So, in practice, we have a simple problem of an object rolling down an angled plane, but interestingly, that angle is changing in time.

To fulfill the condition for rolling without slipping, a static friction force F_s is applied at all times at the contacting site of the sphere with the surface, since that point always has null velocity during the rolling movement. According to Newton's second law for translation and rotation, where m stands for the mass of the sphere, I is its moment of inertia, F_{xi} any applied force along the x-axis, τ_j any applied torques, a_x the linear acceleration and α the angular acceleration, the total forces and torques acting on the sphere are:

$$\begin{cases} \sum_i \mathbf{F}_{xi} = m\mathbf{a}_x \\ \sum_j \tau_j = I\alpha \end{cases} \quad (6.2)$$

In Fig. 6.2 are represented the forces acting on the sphere: along the x-axis there is the projected gravitational force, $F_x = mg \sin(\beta)$ and the static friction F_s . Hence, taking the norms of the vector quantities from now on, we can write the equation of motion:

$$m \frac{d^2 x(t)}{dt^2} = F_x(t) - F_s(t). \quad (6.3)$$

Now let us consider the rotational movement, in an attempt to calculate F_s . One starts by taking the sphere at the highest point of the angled surface, as represented in Fig. 6.2. As it rolls down, it executes a clockwise rotation, with a linear acceleration $a_x > 0$ and an angular acceleration $\alpha < 0$. Since the linear and angular accelerations are related through the radius R of the sphere as $\alpha = -a_x R$, and the torque of static friction is $\tau = -RF_s$ (clockwise rotation requires the negative sign again), one can write:

$$\begin{cases} a_x = \frac{F_x - F_s}{m} \\ \alpha = \frac{-RF_s}{I} \end{cases} \implies F_s = F_x \left(\frac{I}{I + mR^2} \right) \quad (6.4)$$

Plugging in Eq. (6.4) the moment of inertia for a sphere $I = \frac{2}{5}mR^2$, one recognizes that the static force has a fixed value proportional to that of $F_x(t)$ at each instant t . Therefore, the system of differential equations to be solved is:

$$\begin{cases} \frac{dv(t)}{dt} = \frac{5}{7}g \sin(\beta(t)) \\ \frac{dx(t)}{dt} = v(t), \end{cases} \quad (6.5)$$

where $\beta(t)$ is the angle of the surface to the horizontal. There are two variables to be solved simultaneously, for each time step: the position of the sphere x and its velocity along that axis, v . Note that the mass of the sphere is not necessary at this point.

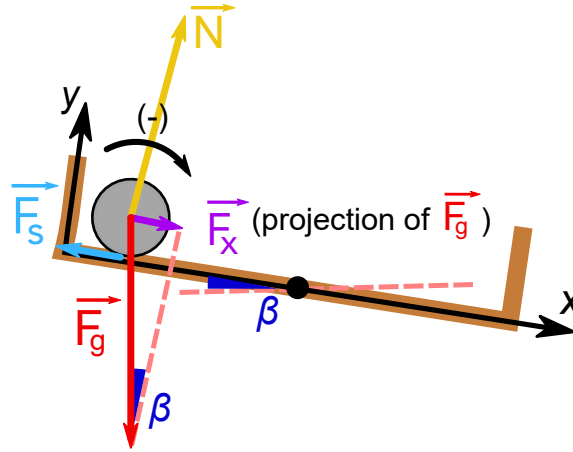


FIGURE 6.2: Diagram of the forces acting on the sphere (F_g and F_s). The angled track is represented in light brown.

We now need to define how the tilt angle of the track varies with time. Since our system uses a servo motor with linear steps, a linear shape for $\beta(t)$ was chosen, with a piecewise definition:

$$\beta(t, A, T) = \begin{cases} \sum_{n=0}^N 4A \frac{t - nT}{T} - 3A, & nT \leq t < \left(\frac{1}{2} + n\right)T \\ \sum_{n=0}^N -4A \frac{t - nT}{T} + 3A, & \left(\frac{1}{2} + n\right)T \leq t < (1 + n)T, \end{cases} \quad (6.6)$$

where $(N + 1)$ is the number of periods that need to be simulated. In short, starting from the position of $\beta(0) = -A$, that is, the track tilted totally to the left, Eq. (6.6) defines a positive slope until half a period T , and maximum amplitude A , and a negative slope the remaining time, until the end of the period, as shown in Fig. 6.3.a for one period, creating a triangular function. This is repeated for $(N + 1)$ periods as expressed by the summation notation. This $\beta(t)$ function is the one that receives the pitch A and the period

of oscillation T that the track is subjected to, making sure the angle varies between $-A$ and A in the specified time interval T .

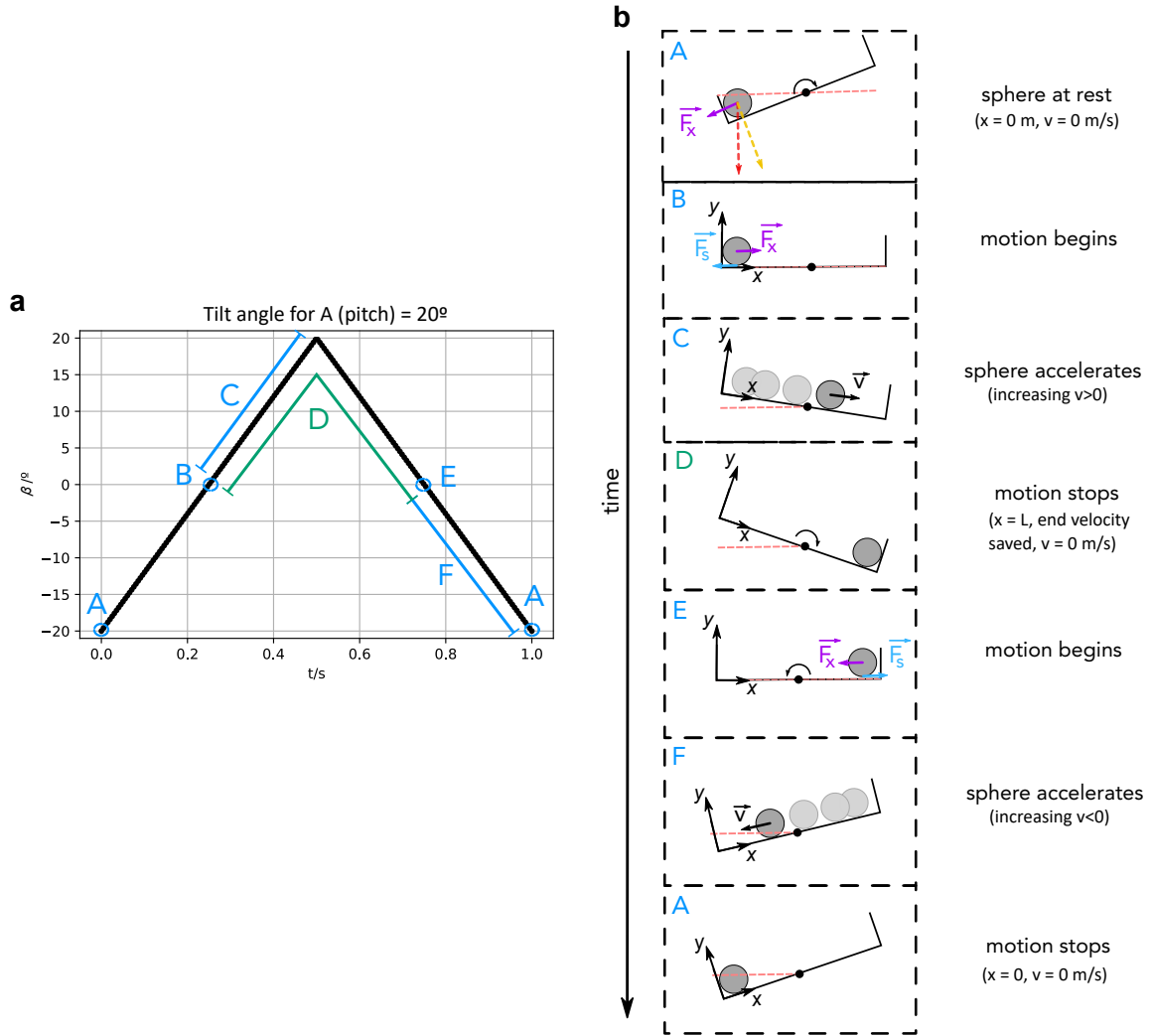


FIGURE 6.3: a) Angle of the tilted track β for one period. b) Scheme of different sphere behaviors according to the track position of the UL-TENG and correspondence to the graph on a).

A typical period of oscillation of the UL-TENG track is represented in Fig. 6.3 for $T = 1$ s and $A = 20^\circ$. The sphere starts at rest at $x = 0$ and $\beta = -20^\circ$, corresponding to point A. The red dashed line represents the gravitational force and the yellow downwards dashed line its projection along the y-axis. In purple is the projection of the gravitational force in the x axis, F_x . The track rotates clockwise from point A to point B. In point B, the resultant force $F_x - F_s$ starts to accelerate the sphere. From this point on, the velocity increases in the positive direction of the x axis, as sketched in C.

Here the timeline can be divided in three cases: the sphere reaching the end of the track before or exactly at $\beta = A$ (D); the sphere reaching the end of the track after $\beta = A$ (D1), when the track is already rotating to the left; and the sphere not reaching the end of the track at all (D2). These two last scenarios are depicted in Fig. 6.4. In all cases, the sphere had its velocity increased with a variable acceleration; however, while in D the acceleration was increasing at all times, in D1 and D2, F_x (and hence the resultant acceleration) started to decrease from the moment the track started to rotate counterclockwise, that is, the moment when β started to decrease from A . Therefore, in the case D1 the sphere does not reach the end of the track with the maximum final velocity possible for that track length, because for that it would need more time to reach the end of the track than the available one, i.e., the half period correspondent to an ever increasing a_x ($\beta \in [0, A]$). In extreme cases, the sphere may not be able to reach the end of the track entirely, which constitutes case D2, as observed tendencially for small amplitudes and low periods of motion.

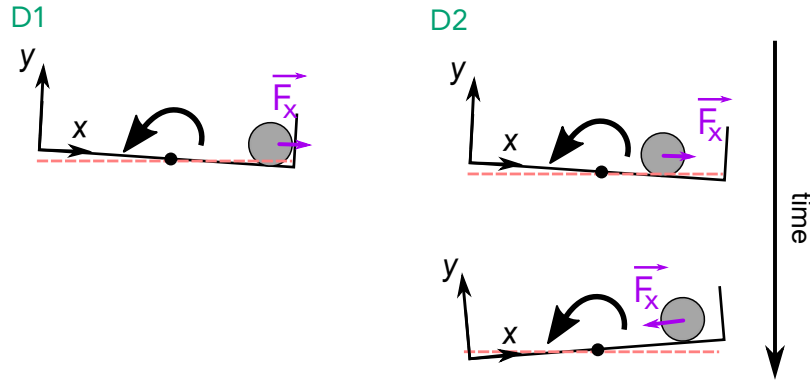


FIGURE 6.4: Other track positions that represent non ideal (maximum velocity not achieved) cases.

When the sphere reaches the end of the track defined as $x = L$, its final velocity is saved and a zero velocity is imposed on the sphere. Note that although the simulation could be extended to an arbitrary number of oscillation periods, only the final velocity of the first collision was saved, provided that it occurred within the total simulation time, $1.5T$.

If the sphere does not reach $x = L$ in $1.5T$, a final velocity of zero is considered. Although there might be in fact (T, A) pairs in which the sphere reaches the end of the track with zero velocity, the momentum transference to the moving part of the UL-TENG would be null in either case, so they both represent an absence of energy generation. It should

be stressed that the simulation computes the sphere position and velocity continuously, so that if a large number of periods N was available, the sphere could in some cases reach the end of the track after $1.5T$. However, the sphere would be so desynchronized with the track, that a negligible amount of collision events comparing to the total observation time would occur. Since that would represent an inefficient harvester, the $1.5T$ total simulation time was maintained.

To solve for the variables $[x(m), v(ms^{-1})]$ from Eq. (6.5) at each instant t , a fourth-order Runge Kutta method was employed. In Fig. 6.5 are depicted sample graphs of position and velocity for a track length of 2 cm. Starting from rest, the sphere accelerates towards one end, reaches $x = 2$ cm, where it remains at rest until the track is tilted enough. From that point, it moves towards the origin (in the opposite direction as the previous movement) with increasing velocity again, stopping at $x = 0$, the initial position, and restarts the cycle.

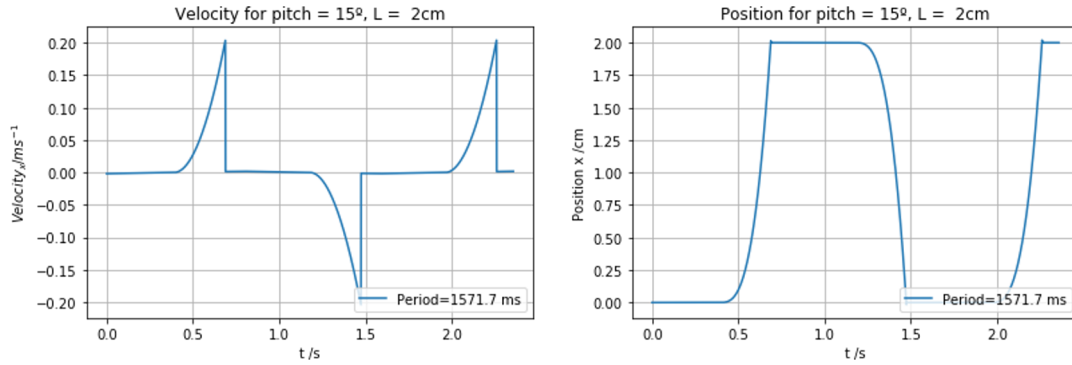


FIGURE 6.5: Sample velocity and position plots for $A = 15^\circ$, $T = 1$ s and track length of 2 cm.

The range of values simulated for each parameter (L, T, A) was chosen considering the experimental measurements. The pitch amplitude was made to vary from 5° to 45° , in steps of 5° . On the other hand, a larger span of 30 periods, from 250 ms to 7 s, with logarithmic resolution, was used to better visualize the final velocity for lower periods. Since these cases are connected to smaller tracks, the array of track lengths had better resolution for lower values: it started with the sequential values [1, 2], then [5,30] in steps of 5 and [40,300] in steps of 10 cm. The final velocities obtained were organized in a (T, A) 3D map for each track length as represented in Fig. 6.6. For a fair comparison, the map colors for all L were normalized to the highest and lowest displayed values.

From the maps it is clear that first, the maximum final velocity increases with L , and second, the region of higher final velocity is situated towards the middle right of the map,

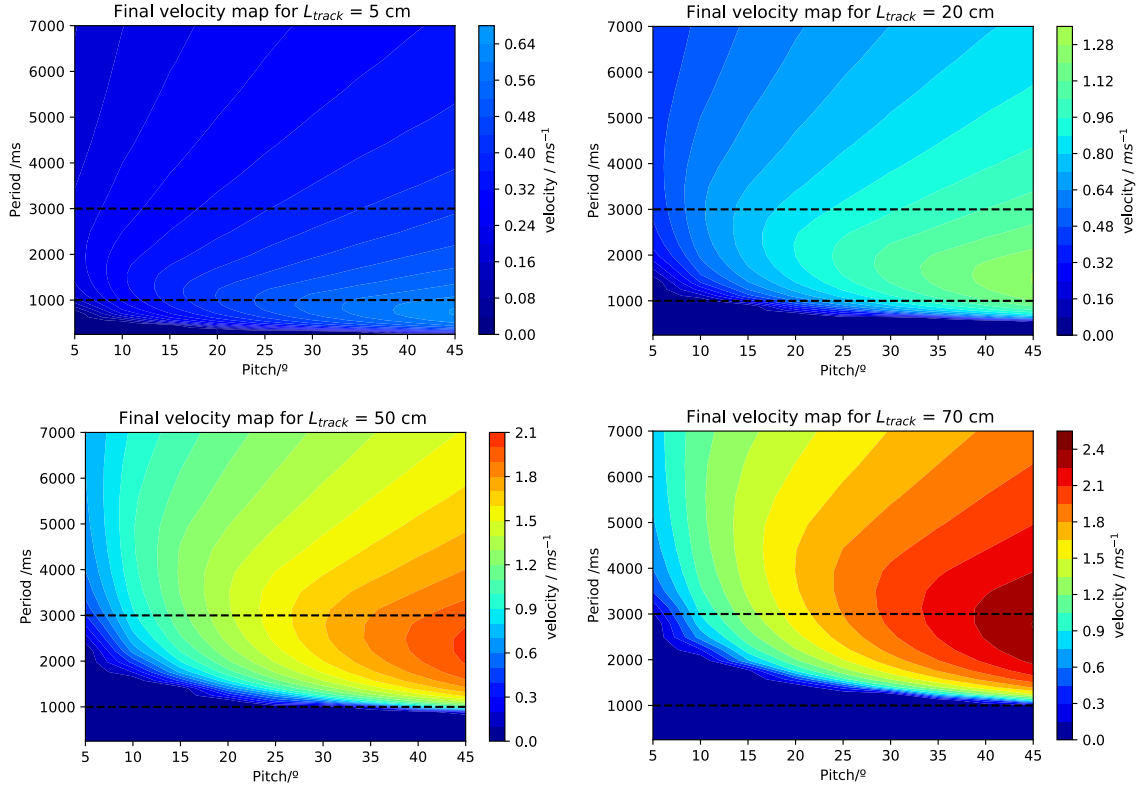


FIGURE 6.6: Impact velocity maps for different track lengths: 5, 20, 50 and 70 cm. The black dashed lines represent the maximum and minimum periods tested in the experimental section.

of high pitch and low period, or if considering only the parameters used experimentally delimited by the dashed line, towards the bottom right of that region. For the lowest periods, the sphere may not reach, or reach with a null velocity, the end of the track at any pitch, as represented by the dark blue color that corresponds to zero final velocity. Interestingly, as L increases, the region of higher velocity seems to move upwards, towards higher periods. This trend was also observed experimentally, in terms of power, as described in section 5.4.

To better understand the importance of period of motion, the final velocity was plotted as a function of T for different A and L as represented in Fig. 6.8. One can observe that the velocity dependence on the period is not monotonous, increasing abruptly until a maximum is reached and decreasing slowly afterwards. This implies the existence of a best period for each pitch and track length that maximizes the final velocity. It is also noticeable that there is a minimum period for the velocity to start having non zero values (i.e., a cutoff period). The best and cutoff periods are represented in Figs. 6.8.a and 6.8.b, respectively.

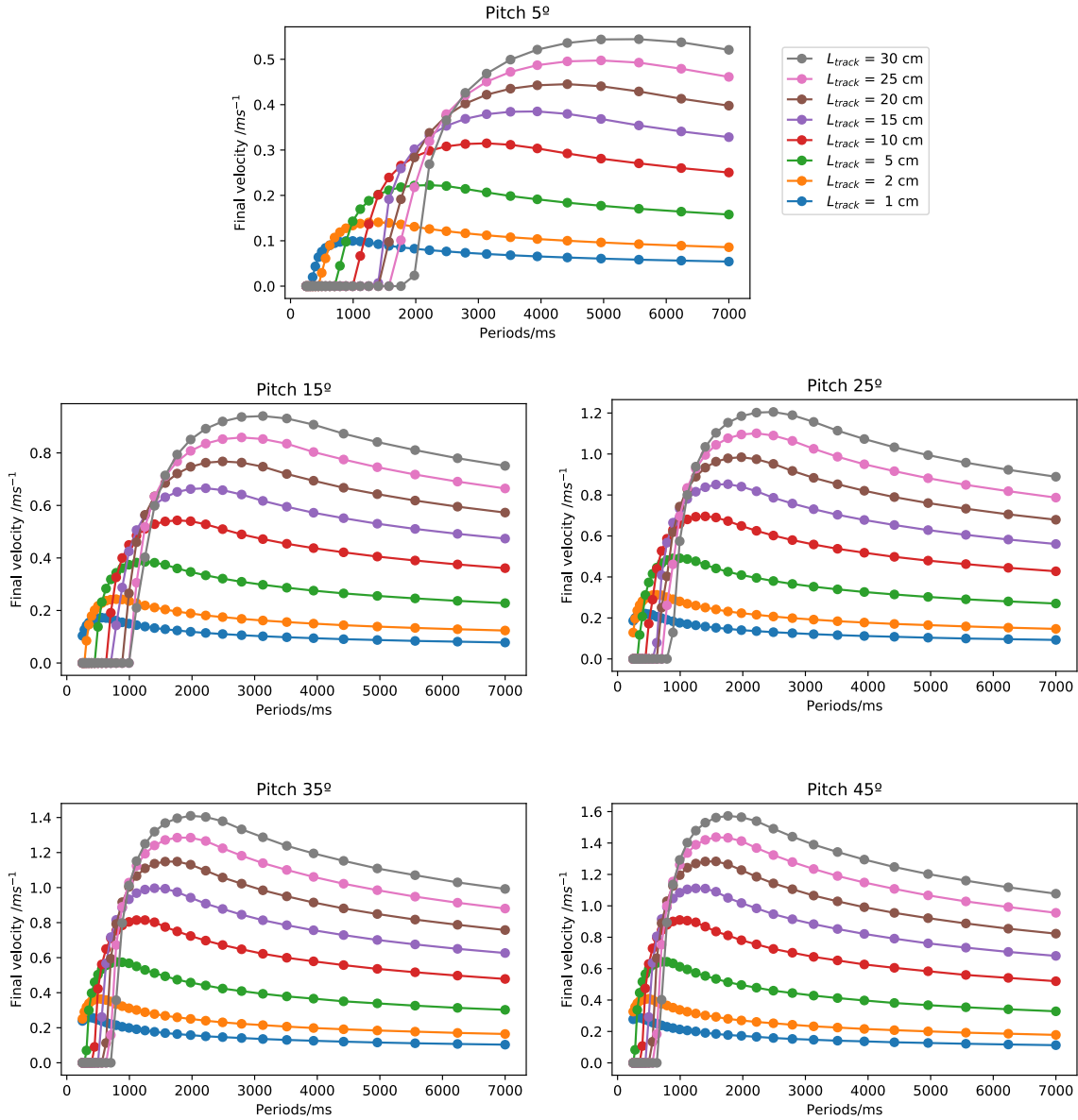
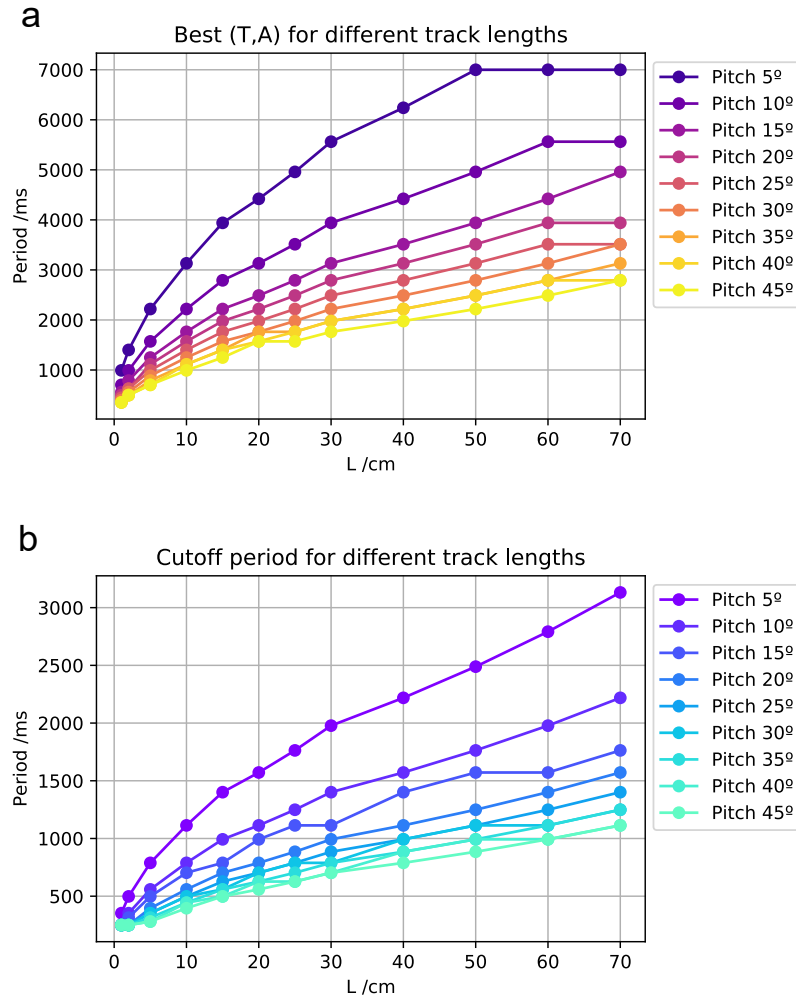


FIGURE 6.7: Study of the sphere final velocity as function of period for several track lengths and pitches.

The best period increases with the track length and decreases with pitch amplitude. In fact, the higher the pitch, the smaller the variation of the best period between different track lengths and for each track length. This means that the best operation condition will be less affected by period variations the higher the pitch is, or in other words, higher pitches are more suited to collect energy from all periods. For this reason, and because the best period values were already leaving the selected range of periods for small pitches (5 and 10°), as evidenced by the predicted best period for those pitches and lengths of 50, 60 and 70 cm being the same (and because for longer tracks more resolution on the region of high pitch would be needed), this study of period (Figs. 6.7 and 6.8) was made only up

FIGURE 6.8: Best period (a) and cutoff period (b) for each A and L .

to 70 cm.

The cutoff periods provide other valuable information: the minimum period for each pitch and track length to have a non-zero output. From the graph of Fig. 6.8.b, it is possible to choose a track length that guarantees, for a sea state (T, A) , that the sphere will always reach the end of the track. For instance, for $(2500 \text{ ms}, 10^\circ)$, all track lengths satisfy that condition, since the cutoff periods for all track lengths are under 2500 ms, but for $(1500 \text{ ms}, 10^\circ)$, only track lengths smaller or equal to 30 cm can be used if one wishes to avoid operating points with zero output.

And how does the pitch influence the final velocity? Performing a similar analysis to the one represented in Fig. 6.7, exchanging T and A , we find that the final velocity always increases with A , for each T and L . Therefore, the maximum pitch in study will always be the one yielding the best results. In fact, even from the 3D maps in Fig. 6.6 we could see that pitch is a determinant parameter, since there is a higher gradient on the final velocity

along the horizontal direction, the pitch axis, than along the period axis.

If there is a best T for each track length and pitch, and the best pitch is always the maximum, then we only lack the investigation of the best track length. In fact, this is the parameter, among the three under study, that can be more easily tuned, simply at the stage of fabrication. In Fig. 6.9 are represented the obtained results for track lengths from 1 cm to 3 m.

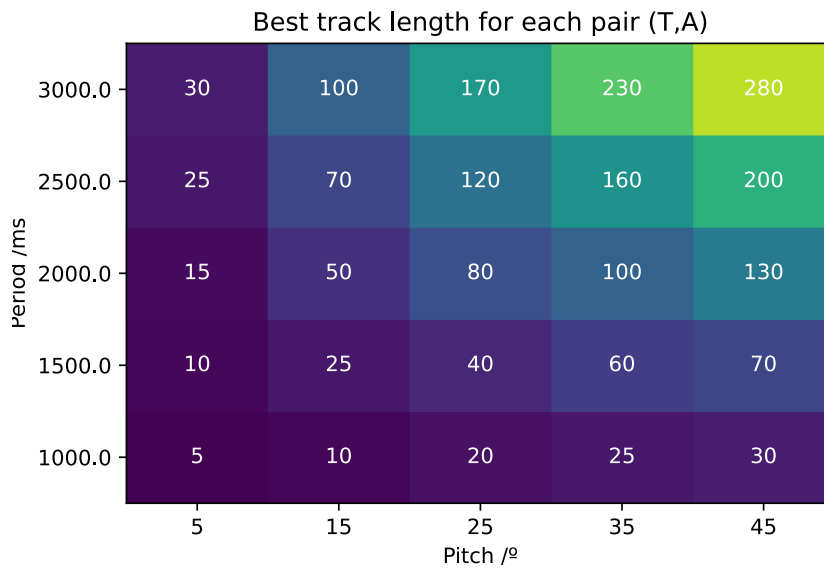


FIGURE 6.9: Best track length (L), in cm, for each pair of period and amplitude, as calculated from final velocity.

As expected, longer tracks are better suited to harvest longer periods, since the region of high velocity moved upwards on the (T, A) map when L was increased. Note that for each (T, A) there really is a configuration, correspondent to a specific track length, that maximizes the sphere impact velocity - and therefore power.

Comparing this map with the experimental map in Fig. 5.10, we see that they coincide in the best track length determination for 4/5 pairs of period and amplitude. The majority of the experimental map points to 20 cm as the best track length simply because there were no longer tracks. This again suggests a relation between the velocity of the sphere, that transfers its momentum to the mobile part of each generator, and the power generated by the UL-TENG.

6.2 Electrical performance of the UL-TENG

To probe how the closing speed of the triboelectric layers affected the generated current, voltage and electric power, two approaches were taken: solving the capacitive model for the CS mode, and using a finite element method with COMSOL Multiphysics® to better recreate the UL-TENG geometry. Note that only the generator at one side is simulated, since the two sides are equivalent.

The capacitive model was chosen instead of the more accurate DDEF model, because we believed the dependence of power on velocity would not be affected by the model choice, since for the used parameters of table 6.1, they differ only on the amplitude of current and voltage for each resistance. Moreover, the DDEF model is much more time consuming and computationally hungry, on a par with COMSOL Multiphysics® - that is already the most faithful representation of the nanogenerator operation.

6.2.1 Modelling with COMSOL Multiphysics®

Given that our nanogenerator did not possess parallel layers, as the CS mode describes, a finite element method was used to more faithfully simulate its operation, more specifically, a COMSOL Multiphysics® model was created. The drawn geometry is composed of 5 domains: the triboelectric layers made of Nylon and PTFE, silver electrodes and a surrounding air domain, as shown in Fig. 6.10. The geometry was built to agree with the parameters used for the CA model presented in table 6.1. Note that although the model is 2D, the finite element method is only valid for finite volumes, therefore a constant thickness equal to W , along the direction perpendicular to the paper/screen, was specified for all geometry domains. This way, the computing time is decreased dramatically, without any loss of accuracy due to the rectangular geometry of each generator.

Concerning the movement of the top layer, a rotation of angle $\alpha(t)$ was applied, so that the displacement for all points is given by:

$$\begin{bmatrix} dx \\ dy \end{bmatrix} = \begin{bmatrix} \cos[\alpha(t)] & -\sin[\alpha(t)] \\ \sin[\alpha(t)] & \cos[\alpha(t)] \end{bmatrix} \begin{bmatrix} x \\ y \end{bmatrix} - \begin{bmatrix} x \\ y \end{bmatrix}. \quad (6.7)$$

By construction, the generator started opened, with an initial angle between layers of 5° , so that the maximum distance between the tips of the static and mobile part is 2.18 mm. These values were tailored by experimental observations and by the ability of COMSOL

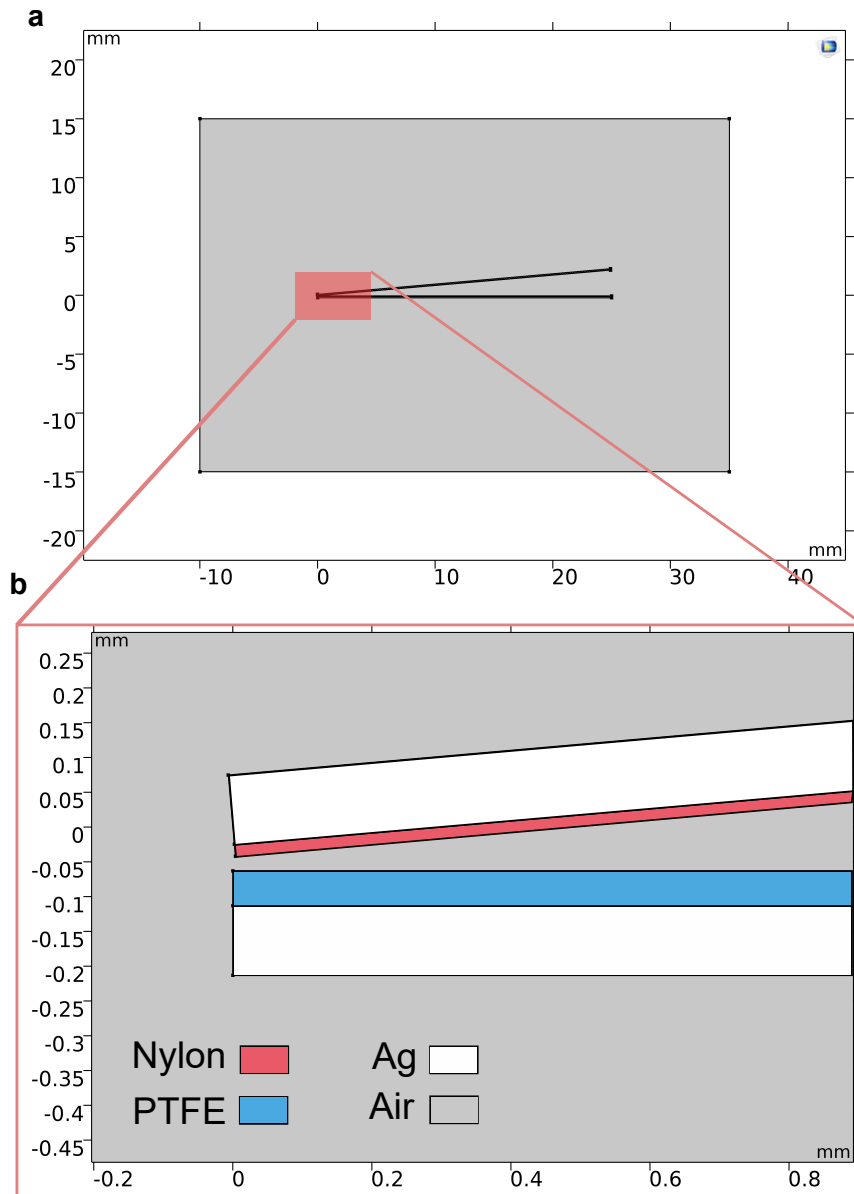


FIGURE 6.10: a) UL-TENG generator with mobile and static parts as drawn in COMSOL Multiphysics®. b) Zoom of the left corner of the geometry, evidencing the materials selected.

Multiphysics® to converge without an abnormal mesh distortion: much higher separating distances would compromise the feasibility of the simulation in terms of increasing time and complexity.

Nonetheless, the displacement of each point (dx, dy) as defined in Eq. (6.7) depends on the displacement of the angle itself: therefore, the function $\alpha(t)$ provided to COMSOL Multiphysics® needed to start at 0° and to take negative values up to -5° , meaning the first half cycle corresponds to contacting the triboelectric layers, closing the TENG. Closing first or opening first will not have an impact on the results, but will be necessary to

understand the temporal correspondence between $\alpha(t)$ as COMSOL Multiphysics® understands it and the output voltage.

The period of the $\alpha(t)$ function was calculated so that the closing velocity at the center of the layers (at the half point of their length) was the closing velocity v_i . This results in the closing/opening velocity being constant in time, changing only in space, along the mobile part. The minimum and maximum values for the closing velocity v_i to be tested were retrieved from the motion simulation presented in section 6.1 plus the sphere - mobile part of TENG collision: for track lengths from 5 to 20 cm, a minimum of 0.25 ms^{-1} and maximum of 4 ms^{-1} were obtained.

Our model required three COMSOL modules: *Electrostatics*, *Electrical Circuit* and *Moving Mesh*. The *Electrostatics* module computes the electrostatic potential in all finite elements for a specific instant of time and correspondent modified geometry (modified by *Moving Mesh*), and the *Electrical Circuit* uses that information to calculate the electric current flowing through the load. From the current, the power output is calculated, again using Eq. (2.9).

To make the domains displacement possible, two similar modules are available: *Moving Mesh* and *Deformed Geometry*. Both were tested, but after realizing the latter permitted the addition or removal of material when displacing the mesh elements [106], the first one was preferred. For the mobile part to rotate, the displacement function in Eq. (6.7) was applied through the conditions *Prescribed Domain* to the upper domains interior and *Prescribed Mesh Displacement* to their boundaries (see Fig. 6.11.a, in blue). To allow for movement to occur inside the air domain, a *Free Deformation* condition was needed for that domain (see Fig. 6.11.a, in green). Note that the triboelectric layers are never in contact in this model, since the mesh elements correspondent to the air in between the two would have to shrink infinitely. This would lead to mesh related errors and inconsistencies, plus dragging and distorting the mesh elements. Instead, a minimum separation of $5 \mu\text{m}$, one order of magnitude lower than the layers thickness, was defined.

The mesh size was set to *Finer* (the 3rd most fine option from a set of 5 options finer than the *Normal* mesh). Starting from this overall definition, the best quality mesh was obtained for the *Physics Controlled* meshing sequence, that allows the mesh builder to adjust the elements size locally, such as at sharp edges where fringing fields will occur (see Fig. 6.11.b). Nonetheless, to prevent the formation of inverted mesh elements (elements so distorted their volume becomes negative) or highly (de)compressed mesh elements

derived from the rotation, an *Automatic Remeshing* condition was added to the *Time Dependent Solver*. This allowed the creation of new, better quality and undistorted meshes during runtime, anytime the distortion was higher than the default value of 2 (reduced to 1.8 for some resistance values), where 0 would mean no distortion. With much higher values, no remeshing would occur for this model, while if this limiting value was too low, a significant computation time would be spent remeshing, and worse, the new mesh could still be a little distorted and fulfill the remeshing condition again, entering an infinite loop that causes the computation to stop. These difficulties were found and surpassed with the aforementioned values. In overall, the minimum mesh element quality registered (from 0 to 1) was 0.3801 (a reasonably high value considering the aspect ratio of the geometry and variability of the elements size) and the average element quality was 0.8048.

From the *Electrostatics* module, a constant *Surface Charge Density* condition was applied on the inner surface of the triboelectric layers, assuming the charge value is already the saturation value (see Fig. 6.11.c in light red). This charge density is related to the displacement field above and under the surface $\mathbf{D}_2$ and $\mathbf{D}_1$, respectively, as:

$$\rho_s = \mathbf{n} \cdot (\mathbf{D}_1 - \mathbf{D}_2), \quad (6.8)$$

where $\mathbf{n}$ is the normal unit vector to each surface.

The *Ground* for the electrostatic potential was defined at the boundaries of the air domain to approximate the zero potential at an infinite distance condition (see Fig. 6.11.d in purple). The two inner surfaces of the electrodes (in contact with the triboelectric layers) were given a *Terminal* condition (see Fig. 6.11.c in dark red), so that a charge Q_I is allowed to build (be induced) on those surfaces, according to the equation:

$$Q_I = \oint \mathbf{D} \cdot \mathbf{n} dS. \quad (6.9)$$

The *Electrical Circuit* module assures the connection of the terminals through a variable resistor. It computes the electrical current on the resistor according to the charge induction at the electrodes (the terminals):

$$\frac{dQ_I}{dt} = I_{cir}. \quad (6.10)$$

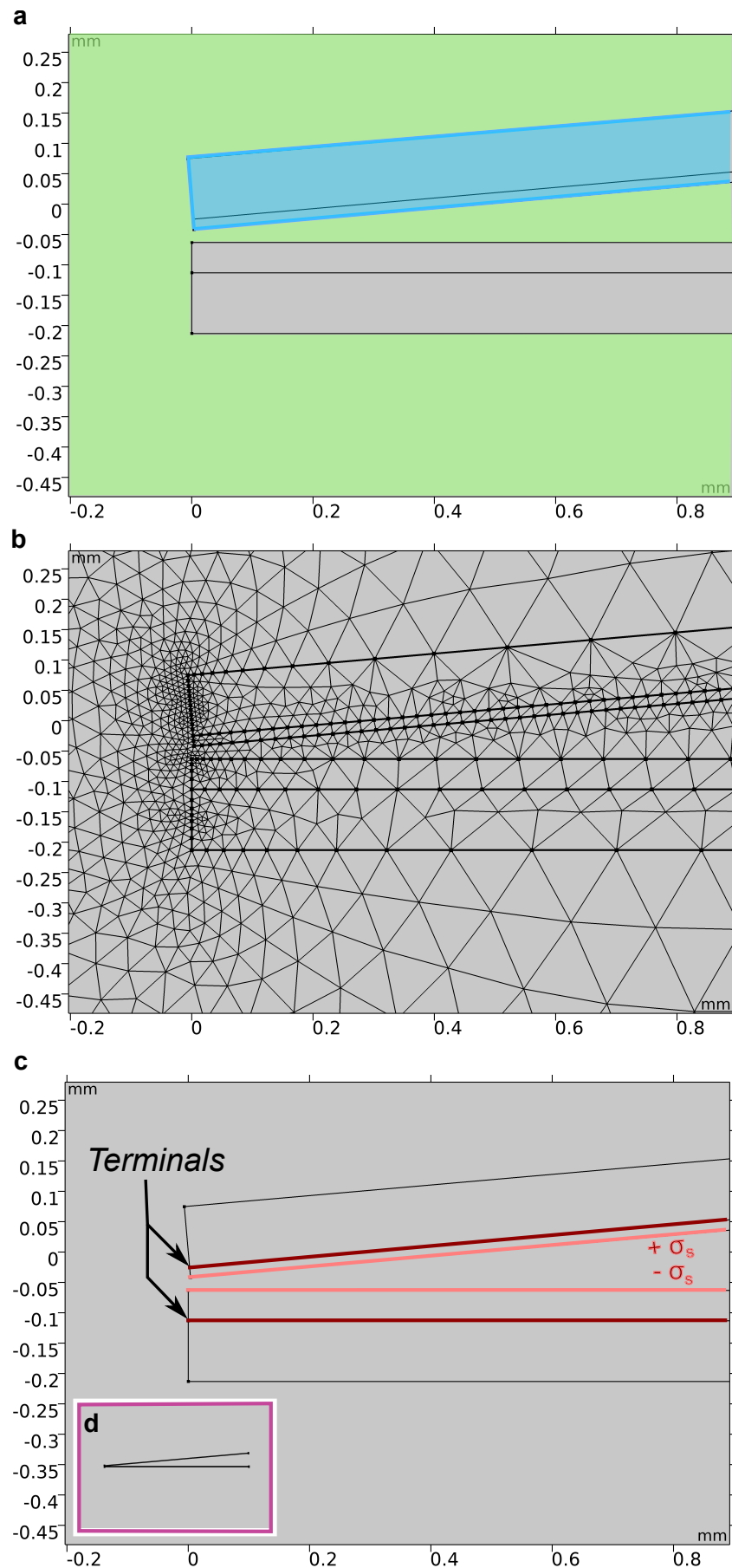


FIGURE 6.11: COMSOL Multiphysics® model geometry highlighting the: a) *Moving Mesh* conditions; b) Sample of the mesh created; c, d) *Electrostatics* module conditions.

Concerning the solver sequence, a robust and consistent (important factors due to the high aspect ratio of the geometry) method was chosen, although more RAM and time consuming [107]: the *Direct Time Dependent Solver* together with the *Fully Coupled* approach. The *Fully Coupled* approach forces all the dependent variables and their multiphysics couplings to be included in the same, high ranked, linear system of equations. The *Direct Time Dependent Solver* is the algorithm used to solve the linear system on each iteration, responsible for calculating the solution at each time step. A side note: the solver uses a damped Newton's method, and for this problem it is important the damping factor can be tuned by COMSOL during runtime, choosing the option *Automatic (Newton)* on the *Nonlinear method* menu.

6.2.2 Solution of the COMSOL Multiphysics® model

After this description of the model, let us proceed to the results. Similarly to what was observed in Chapter 2 when the CA and DDEF models were compared, the higher the resistance value, the longer the transient regime, which acquires a significant time duration for resistances larger than $10^7 \Omega$. Although it has a smaller impact, increasing velocity also increases the duration of the transient regime. In fact, most of the resistances were simulated for 4 periods, as represented in Fig. 6.12.a in green: a closing/opening of the mobile part is 1 period, then there is a waiting time for 1.5 periods, then another cycle of closing/opening corresponding to 1 period, then finally half a period of waiting time. However, for the last two resistances, and depending on the velocity value, more than 4 periods were needed to surpass the transient regime. For 31.6 M Ω , 10 periods were needed, while for 100 M Ω , that number was not enough after the velocity of 2 m/s, value after which 30 periods were simulated.

Another observation is the effect of the resistance on the shape of the voltage peaks. As the resistance becomes closer and closer to the open circuit condition, the electric potential peaks in time start to deform due to the shape of the distance between layers function $z_1(t)$, as represented in Fig. 6.12.b. In this case, $z_1(t, x)$ is a function of space as well, due to the declination of the top layers. In fact, the distance between layers is the arc length correspondent to an angle $\alpha(t)$ plus the small vertical height of 5 μm , so that:

$$z_1(t, x) - 5 \mu\text{m} = r(x)\alpha(t) = \frac{\alpha(t)}{\cos[\alpha(t)]}x \approx x\alpha(t), \quad (6.11)$$

where r is the position over an axis coincident with the tilted layer.

This small angle approximation was verified plotting the $z_1(t, x)$ function in COMSOL Multiphysics®, where we saw that, for any pair of points (x, y) , $z_1(t, x)$ has the same shape as the angle function $\alpha(t)$. This way, it is possible to compare the open circuit voltage with the function $\alpha(t)$ instead of $z_1(t, x)$ directly without any loss of generality.

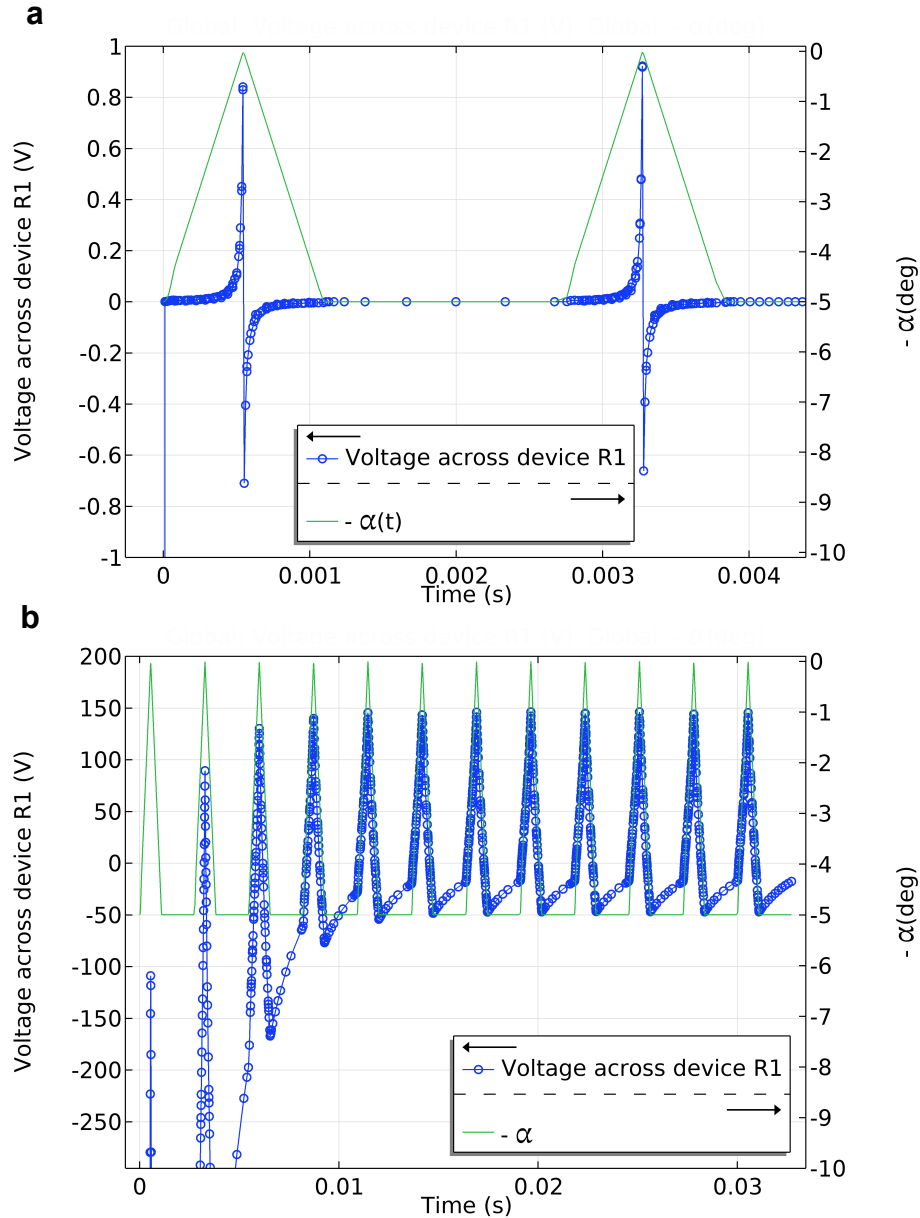


FIGURE 6.12: Voltage peaks compared with the angle between the static and mobile parts of the generator for the same velocity of 2 m/s, as computed by COMSOL Multiphysics® at the resistance of: a) 1 kΩ and b) 100 MΩ.

The distortion of the peaks represented in Fig. 6.12 is gradual, but shown here for 1 kΩ (Fig. 6.12.a) and 100 MΩ (Fig. 6.12.b) for greater contrast. It is possible to observe that for 1 kΩ the positive and negative peaks are close to each other and seem to correspond to the minimum separation between layers ($\alpha = 0$). On the other hand, for 100 MΩ the

shape of the peaks is close to the $\alpha(t)$ function shape, with positive peaks corresponding to the minimum separation between layers and the negative peaks corresponding to the beginning of the waiting time, when α returns to 5° and the generator stays open for a while (1.5 periods).

While the CA and DDEF models ran previously showed peaks strictly symmetric in time, in COMSOL Multiphysics® some asymmetry between positive and negative peaks is always present. This might be attributed to the time discretization and/or meshing, plus the deformation explained above for high resistances and velocities, that accentuates that asymmetry.

In total, the model was solved for 11 logarithmically spaced resistance values, from 1 k Ω to 100 M Ω , for 7 values of velocity: [0.25, 0.5, 1, 1.5, 2, 3, 4] m/s. The final current, voltage and power as functions of resistance are presented in Fig. 6.13. Due to the referred asymmetry, these values were calculated from the mean of the positive and negative peak values for all resistances. Note the increase in short circuit current and maximum power due to the increasing velocity, as well as the displacement of the optimum resistance one order of magnitude towards lower resistance values (from 1 M Ω to 31.6 k Ω). Note that both the open circuit voltage values and the short circuit current are higher than what was predicted by the CA model.

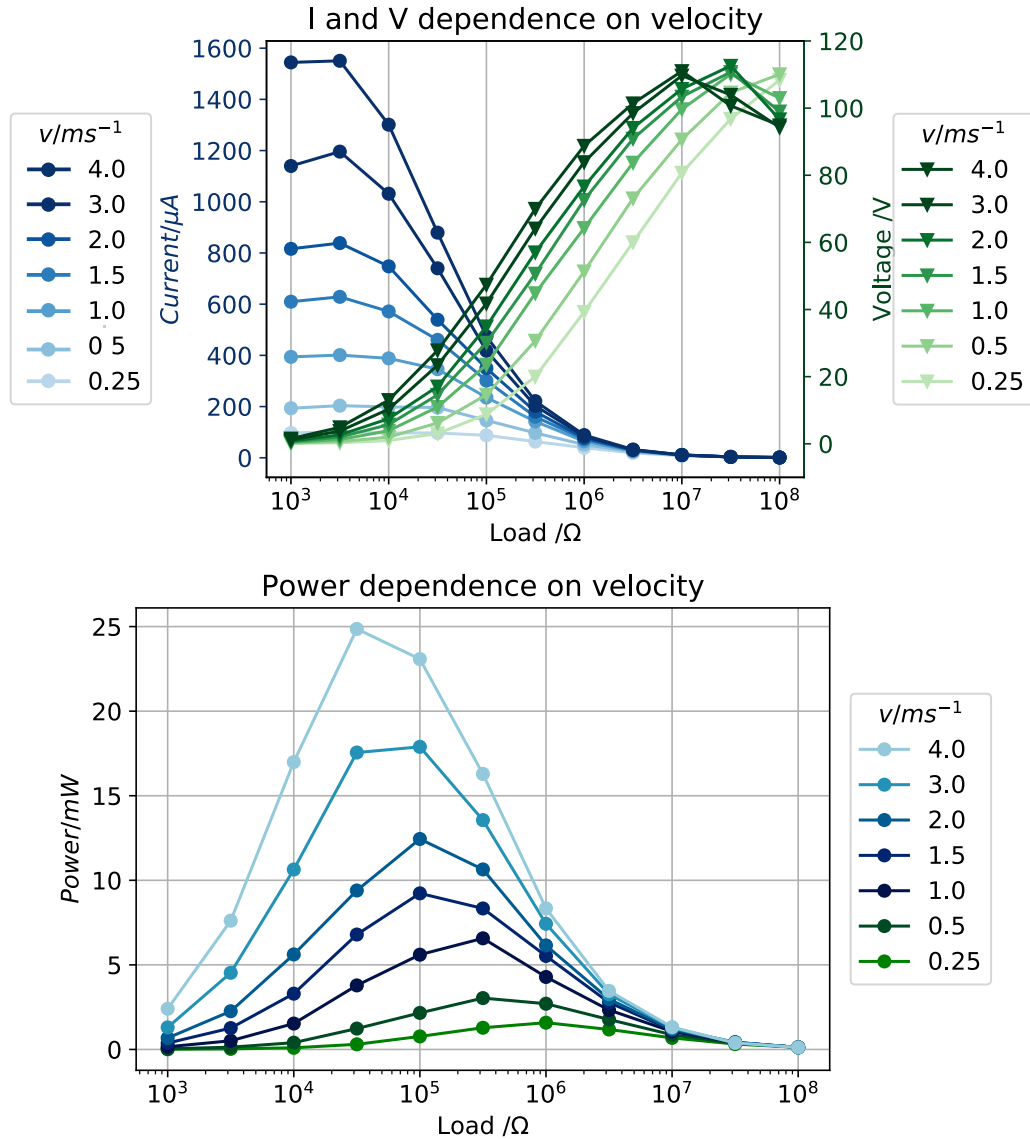


FIGURE 6.13: Current voltage and power dependence of maximum TENG closing velocity calculated with COMSOL Multiphysics®.

6.2.3 Solving the CA model

As described in section 2.3.2, the CA model was solved for the induced charge σ_I , with an order 4 Runge Kutta integrating method. Note that this model is taking into account the CS mode, with parallel layers, an approximation attending to the small rotation angles of the TENG mobile part. Load resistances from $1k \Omega$ to $1G \Omega$ were tested, yielding the electric power through Eq. (2.9), with the parameters presented in Table 6.1.

A sinusoidal function was used as the distance between the triboelectric layers $z(t)$, starting at $5 \mu m$ instead of 0 to better mimic the COMSOL Multiphysics® simulation. The maximum height the top layers can achieve could not be any value; it was calculated to

minimize the difference between the two distance between layers functions, the one used in COMSOL Multiphysics® simulation, $z_1(t, x)$, and the one to be defined for this CA model simulation.

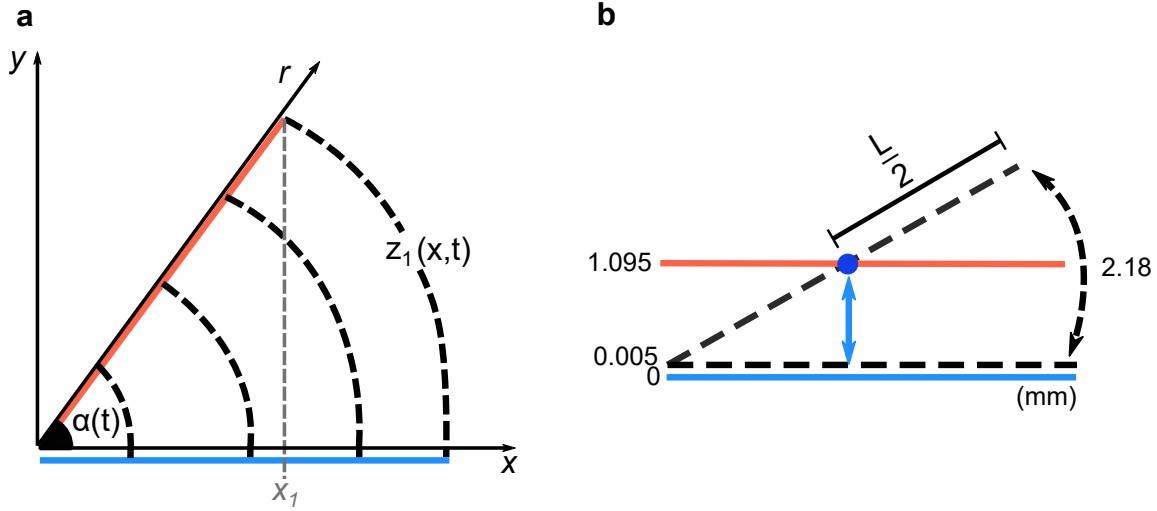


FIGURE 6.14: a) Scheme evidencing the calculation of the mean distance between layers for the tilted geometry. b) Relative position of the always horizontal layer used in the CA model (in blue) compared with the tilted layer used in COMSOL Multiphysics® (in black dashed line).

If the distance (curved, along the arc) of the tilted layer to the bottom layers is $z_1(x, t)$, as defined in Eq. (6.11), the mean distance over x is:

$$\bar{z}_1(t) = \frac{1}{x_1} \int_0^{x_1} z_1(x, t) dx, \quad (6.12)$$

where $x_1 = L \cos[\alpha(t)]$ is the position of the tip of the top layer on the x axis, as represented in Fig. 6.14. From the definition of $z_1(t, x)$ in Eq. (6.11), this results in:

$$\bar{z}_1(t) = \alpha(t) \frac{L}{2} + 5 \mu m. \quad (6.13)$$

Note that this is equivalent to working in polar coordinates, integrating the arc lengths $r\alpha(t)$ along the radial axis from $r = 0$ to $r = L$ $\left(\frac{1}{L} \int_0^L r\alpha(t) dr \right)$. Placing the horizontal mobile layer used in this simulation at the height $\bar{z}_1(t)$, this simulation mimics the motion prescribed in COMSOL Multiphysics® the most faithfully possible, minimizing the discrepancy between the distance between layers functions from each case. For $t = 0$ we find the maximum height of the horizontal layer to be $\bar{z}_1(0) = 1.09$ mm, as drawn in Fig. 6.14.b. Since the height of any point at the tilted layer (along the y -axis) is $y(x) = r \sin[\alpha(t)] \approx r\alpha(t)$, looking at Eq. (6.13), one realizes that the horizontal group

of layers crosses the tilted group of layers at $r = \frac{L}{2}$, at least when the generator is fully opened and closed, as shown in Figure 6.14.b.

Hence, the amplitude of the sinusoidal is $\bar{z}_1/2$, and the period of the function $z_2(t)$ was defined so that the closing velocity v_i was the maximum velocity of the sinusoidal motion, that is, the maximum value of the absolute value of the derivative of $z_2(t)$: $\left| \frac{dz_2}{dt} \right|$. These characteristics of motion are summarized in table 6.2.

Parameter	Value	Parameter	Value
v_i	$[0.25, 4] \text{ ms}^{-1}$	A_z	0.545 mm
T	$\frac{2\pi A_z}{v_i} \text{ s}$	Function $z_2(t)$	$(A_z + 5 \mu\text{m}) + A_z \sin\left(\frac{v_i}{A_z} t\right)$

TABLE 6.2: Movement parameters of the UL-TENG used in the CA model simulation of electric power.

The RK4 temporal step was adjusted according to the convergence for each resistance (since they vary several orders of magnitude). In fact, the lower the resistance, the smaller the step size for the method RK4 to converge (used step sized ranged from $\times 10^{-8}$ to $\times 10^{-6}$ s). On the other hand, the higher the resistance, the longer the transient model, so that a higher final time needed to be chosen, increasing as well the computation time.

After exploring and surpassing this and other limitations of the method, some interesting results were obtained, depicted in Figs. 6.15 and 6.16. Despite the distance between layers being a sinusoidal function, we observe that the open circuit voltage conforms to that shape also, as shown in Fig. 6.15.b (although it is limited by two symmetric values). Concerning Fig. 6.16, we see the short circuit current increasing steadily with the velocity, precisely what Eq. (2.20) predicted, while the open circuit voltage remains unaltered. However, the voltage starts to increase at lower resistances for higher velocities, resulting in the displacement of the power curve towards the region of lower resistances by one order of magnitude (from 3.16 MΩ to 205 kΩ). The maximum power is always increasing with velocity, reaching a more than 5 fold increase over the range of velocities tested.

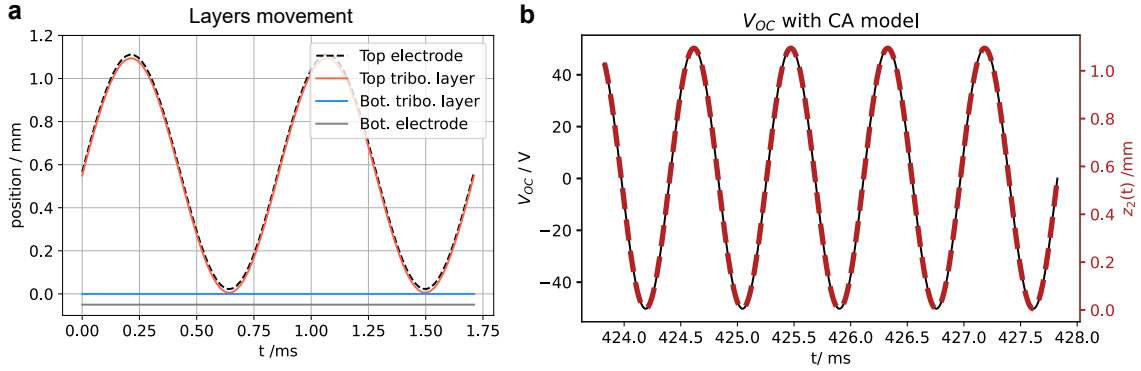


FIGURE 6.15: a) Vertical position of the layers over time of the four layers that compose the triboelectric generator used in the CA model simulation. b) V_{OC} compared with $z_2(t)$ for sinusoidal motion used to solve the CA model.

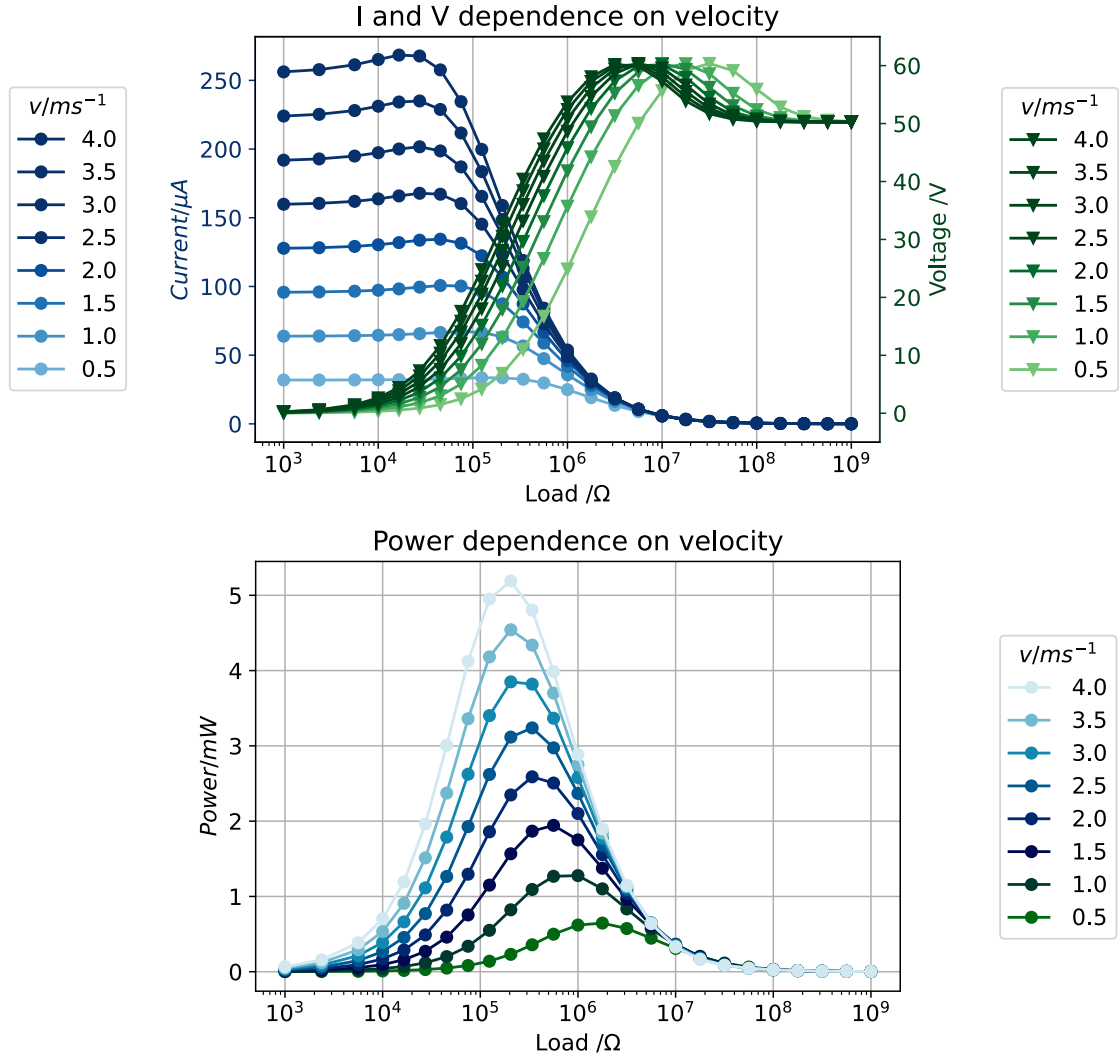


FIGURE 6.16: Current voltage and power dependence of maximum TENG closing velocity calculated with the CA model for a sinusoidal $z(t)$.

Looking at the asymmetries on the power graph (Fig. 6.19.b), we can now understand how velocity affects the output power for each resistance. Slicing the power graph, in Fig. 6.17 are the results for the resistances [1k, 16.5k, 124k, 1M, 10M] Ω .

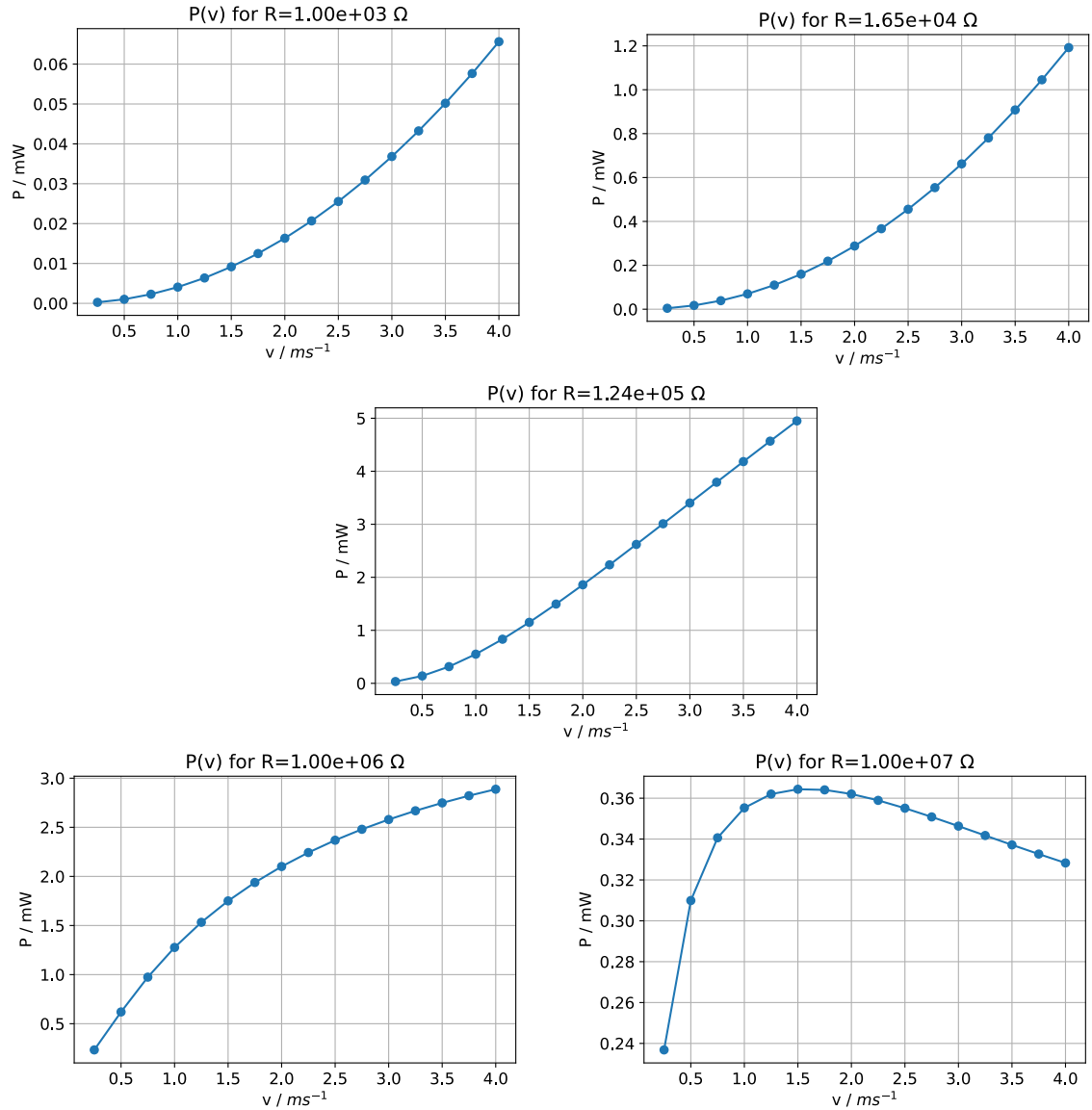


FIGURE 6.17: Power as function of velocity for several resistance values, from top to bottom, left to right: [1k, 16.5k, 124k, 1M, 10M] Ω , as simulated by the CA model.

The function of power in velocity starts with a positive concavity on the first resistances, straightens around 124 k Ω , and then acquires a downward inflexion as evidenced already at 1 M Ω . There is no single resistance where the power is linear; there is always some curvature. However, at the optimum resistance, that varies according to the velocity, that might not be the case, as investigated in the next section.

Considering that the CA model overestimated the values of maximum power relatively to the DDEF model, it is surprising that the results of COMSOL Multiphysics® simulation were even larger not only in terms of maximum power, but also open circuit voltage and short circuit current. In order to investigate why this happened, the CA model was also computed for a triangular $z(t)$ function (see Fig. 6.18.a), in order to be better compared with COMSOL Multiphysics®. Moreover, one must guarantee that, if both simulations were running at the same pace, at the same time, the upper group of layers for each of them would be moving synchronously. Considering that velocity is fixed for each test, choosing similar distance between layers functions for each simulation is important, but only when those functions have the same shape will we guarantee synchrony. This way, the horizontal group of layers from the CA model is always moving with its center coincident with the center of the tilted group of layers, at $r = \frac{L}{2}$: their velocity is equal at all times in this point. In other words, the closing/opening velocity is constant and always equal to v_i (as described in the beginning of this chapter), as opposed to the version with a sinusoidal velocity, whose maximum value was equal v_i .

The open circuit voltage is represented in Fig. 6.18.b compared with the distance between layers $z_3(t)$. In fact, the peaks have also deformed to conform to the triangular shape, just as it happened in the COMSOL Multiphysics® simulation.

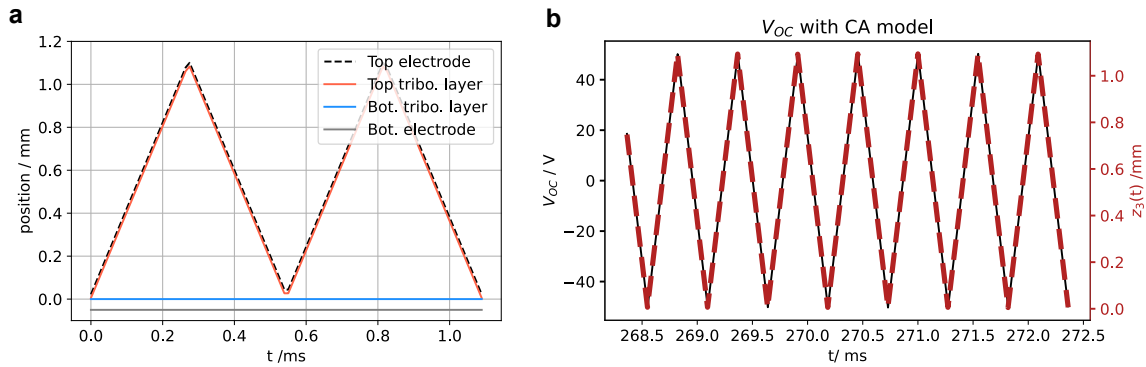


FIGURE 6.18: a) Position of the layers and b) V_{OC} compared with the triangular $z_3(t)$ used to solve the CA model.

As for the complete results of voltage, current and power (see Fig. 6.19), a major difficulty appeared on the lower resistances region. The optimum resistance was greatly deviated towards lower values, so that it became computationally extensive to reach the short circuit current (step sizes as small as 10^{-10} were tried). Nonetheless, it was possible to analyze the maximum power, that steadily increased with velocity as previously observed, and the open circuit voltage, that remained unaltered despite the change in shape

of $z_3(t)$. An important change is the range of optimum resistances, that now lies between 16.5 k Ω and 205 k Ω .

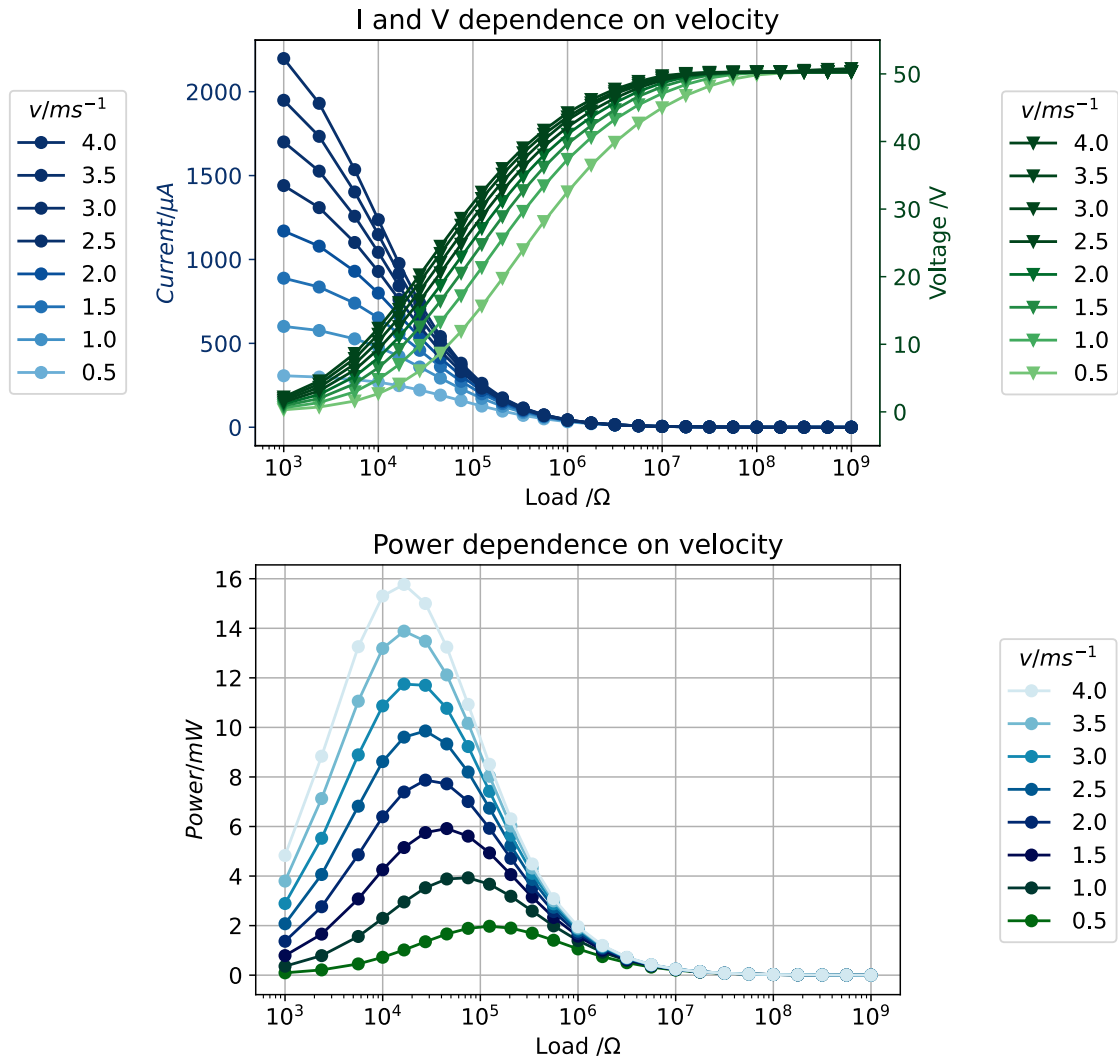


FIGURE 6.19: Current, voltage and power dependence of maximum TENG closing velocity calculated with the CA model for a triangular $z(t)$.

6.2.4 Comparison of the two approaches

Although power is not always an increasing function of the velocity, as seen for high resistances, our region of interest is around the optimum resistance as real applications will track that operation point. Therefore, Fig. 6.20 plots the maximum power for each velocity (at each optimum resistance), obtained with COMSOL Multiphysics® and the CA model for the case of (a) sinusoidal motion and (b) triangular motion. We see that both models present a linear increase of the maximum electric power of the generator with the velocity (albeit with different slopes). The triangular motion for the CA model,

as expected, describes a behavior closer to what the finite element method calculated, while the sinusoidal motion case has a significantly smaller slope of power on velocity in the considered range of $[0.25, 4]$ m/s. In the literature, most reports show an increase of power on velocity [52, 53] (sometimes hidden on another parameter, the frequency), but do not dwell into the shape of this increase. The fact is, indeed maximizing the velocity will contribute to the maximization of power. It now becomes clear why the experimental power maps presented in section 5.4 and the final velocity maps from section 6.1 showed similar regions of maximum power/maximum final velocity, respectively.

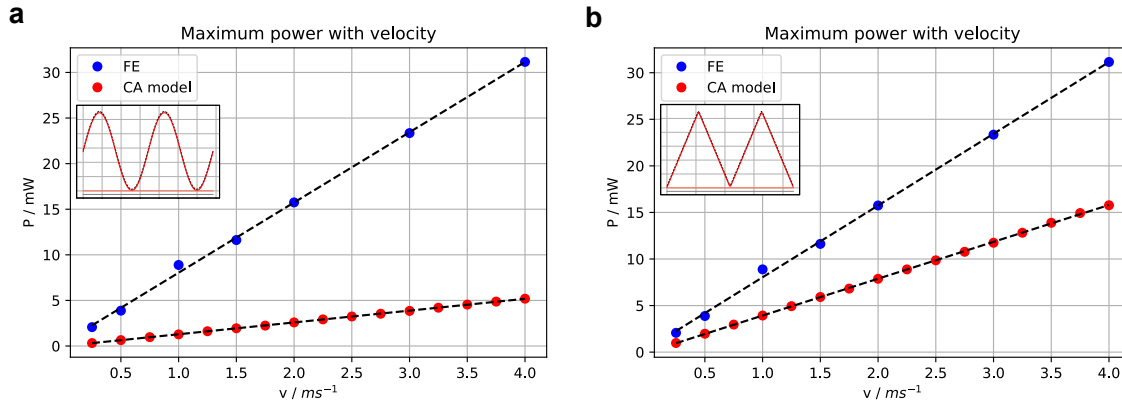


FIGURE 6.20: Comparison of maximum power as function of velocity as obtained by the simulation on COMSOL Multiphysics® and by the CA model with motion of the layers $z(t)$: a) sinusoidal; b) triangular.

Another point of comparison between the models is the open circuit voltage shape. While the COMSOL Multiphysics® simulation had the peaks deform to conform to the distance between layers function (that is always positive), this behaviour was completely absent from the CA model. The latter calculates an open circuit voltage always between symmetric values, i.e, offsetted from the distance between layers $z_2(t)$ or $z_3(t)$. This occurs even though it attributes the open circuit voltage designation to the expression $\frac{\sigma_S z(t)}{\epsilon_0}$, implying it should vary between 0 and over 6000 V for the parameters used in the simulation [see Eqs. (2.21) and (2.23b)]. In fact, this behavior (V_{OC} being all positive) has been reported for simulations of the CA model [43].

It is interesting to realize that the variation of the optimum resistance is inversely proportional to the velocity, as described in section 2.3.2. This justifies the results obtained in section 5.4.2, since (3000 ms, 15°) and (1000 ms, 45°) are two pairs (T, A) that correspond to two very different sphere velocities. The higher final velocity pair [(1000 ms, 45°)] corresponds to an optimum resistance of the TENG deviated towards lower resistances when

compared to the pair of lower velocity [(3000 ms, 15°)], as seen on this section. In Fig. 6.21 is represented the optimum resistance as function of velocity and a fitting curve for each simulation: (a) CA model with triangular motion and (b) COMSOL Multiphysics®.

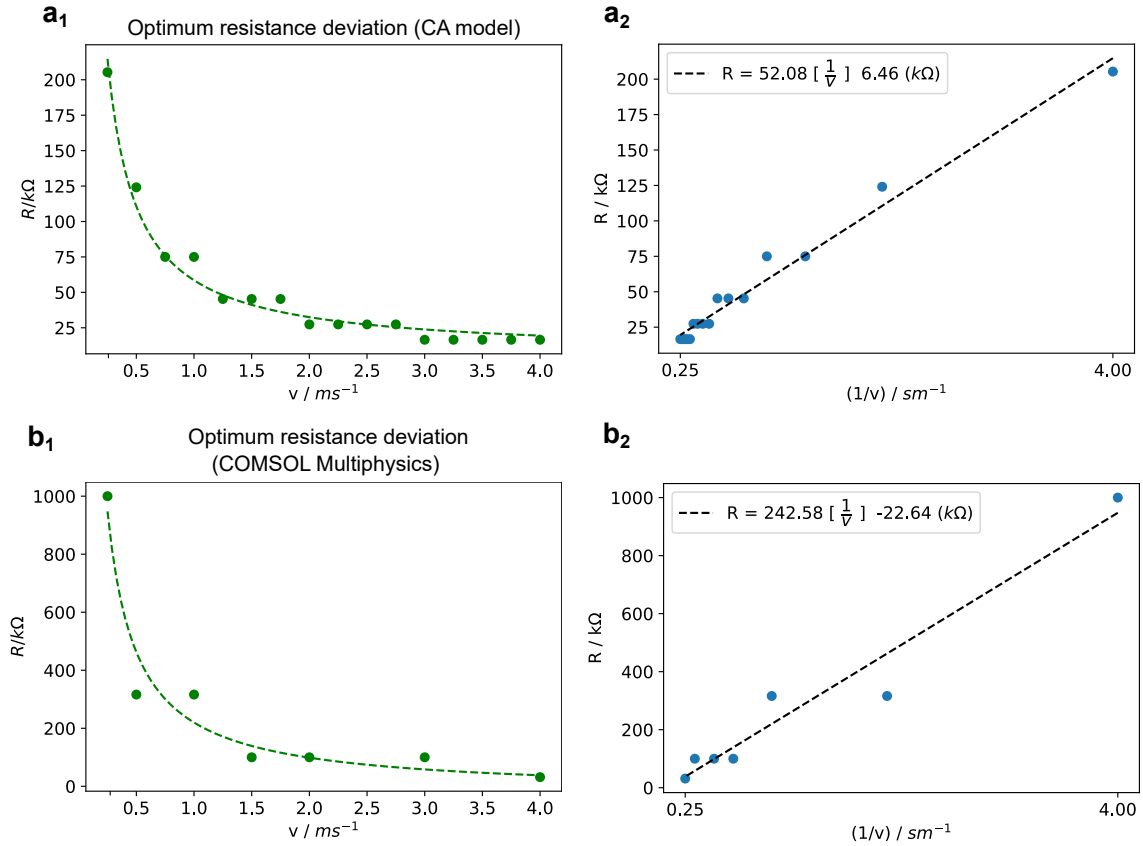


FIGURE 6.21: (1) Optimum resistance as function of velocity and (2) fitting line to the linearized data, for the simulation done with a) CA model with triangular motion; b) COMSOL Multiphysics®.

The first observation that can be made is that the range of values of the optimum resistance is significantly different in the two models. Despite the maximum power predicted by the COMSOL Multiphysics® simulation being close to the CA model with the triangular motion, the latter predicts a much lower range of optimum resistance (16.5 to 205 kΩ) compared with COMSOL Multiphysics® (31.6 kΩ to 1 MΩ). This could indicate that the tilting of the layer, which constitutes a fundamental change in the geometry of the nanogenerator, despite generating more power, must impose a higher internal capacitance relatively to the horizontal case, causing the optimum resistance to increase.

This inverse proportionality dependence means that the optimum resistance will eventually saturate at a low value. In the case of the CA model, the optimum resistance will saturate at $6 \pm 3 \text{ k}\Omega$, as shown on the fitting parameters in table 6.3. On the other hand,

the COMSOL Multiphysics® simulation has a negative horizontal asymptote, indicating that an insufficient number of resistances has been calculated. Another consequence of this dependence is that significant changes in optimum resistance occur for small velocities. Therefore, the higher the range of contact/separation velocities that a nanogenerator works on, the more stable the value of the optimum resistance will be.

Equation	Simulation	$m \pm \Delta m$ (kΩ)	$\frac{\Delta m}{m}$ (%)	$b \pm \Delta b$ (kΩ)	$\frac{\Delta b}{b}$ (%)	R^2
$R_{opt} = m \left(\frac{1}{v} \right) + b$	CA model	52 ± 2	4%	6 ± 3	40%	0.98
$R_{opt} = m \left(\frac{1}{v} + b \right)$	COMSOL Multiphysics®	243 ± 26	11%	-23 ± 46	202 %	0.95

TABLE 6.3: Fitting parameters of the optimum resistance dependence on velocity for the CA model and COMSOL Multiphysics® simulations.

6.3 Generated energy by the UL-TENG

Usually, power is taken as the electrical quantity of election when describing the performance of TENGs. However, the question arises whether, even if a certain pair (T_1, A_1) has power peaks lower than another (T_2, A_2) , can T_1 be small enough so that the total energy for a certain time interval surpasses that of the operating point (T_2, A_2) ? In order to investigate this, a new set of simulations that combined the previous two was performed.

Firstly, the final velocity array for the selected periods and pitches was calculated and saved. After being converted to the closing velocity values through Eq. (6.1), the CA model power simulation was performed for each of those values, at the corresponding optimum resistance from the data fit made in section 6.2.4 and using the triangular distance between layers function. This was repeated for track lengths from 1 cm to 3 m: in this range, the closing/opening velocities fall in the interval $v_i \in [0.19, 14.06]$ m/s, correspondent to optimum resistances in the interval $R_{opt} \in [10.2, 279]$ kΩ.

The energy per cycle was calculated as the integral of the power function for one cycle, represented over the right column of Fig. 6.22. Since each of the velocity values has a period associated, knowing the number of cycles in a fixed time interval (60 s) is enough to compute the total energy from the energy per cycle. Then, each result of total energy is traced back to the velocity it corresponds and in its turn, the velocity is traced back to the period and amplitude that originated them. This way, it is possible to build total energy (T, A) maps, as represented in Fig. 6.23.

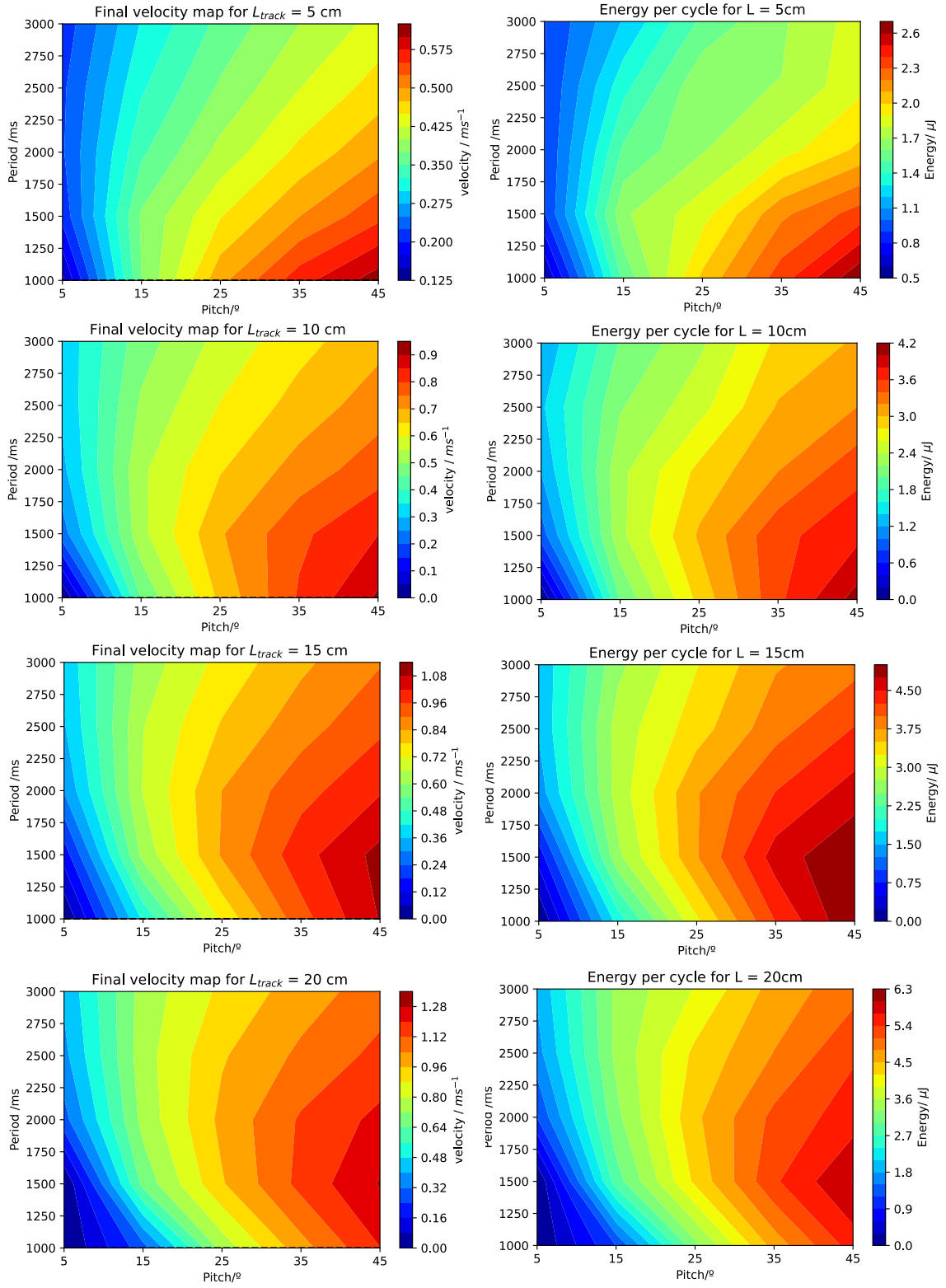


FIGURE 6.22: Non-normalized plots, for the set of parameters used experimentally, of simulated: a) final sphere velocity; b) energy generated per cycle.

Note that the energy per cycle distribution on the (T, A) map follows almost flawlessly the final velocity plots, here represented for periods between 1 and 3 s and the track lengths experimentally available. This means that not only increasing velocity increases the peak power, as a higher peak power implies a higher integral of the power peak in time, therefore leading to a higher energy per cycle. This was not mandatory, since the peaks could have become slimmer the taller they grew.

Notwithstanding, the total energy suffered a reduction for higher periods: the more waiting time (period of the track motion) between closing/opening cycles of the TENG, the less total energy is generated in the 60 s time interval (for the same peak power). This trend is moderated/accentuated by the power increase/reduction with increasing period, yielding the final results seen in Fig. 6.23.

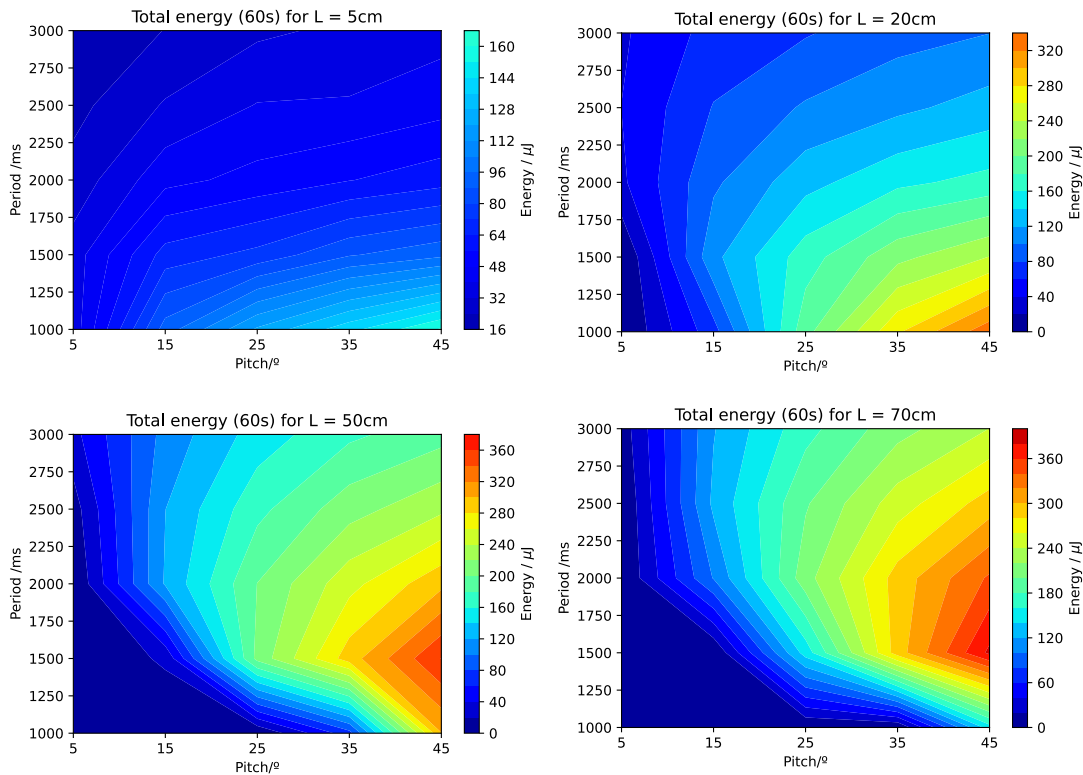


FIGURE 6.23: Normalized plots (to the highest and lowest displayed values) of total energy generated over 60s for track lengths of 5, 20, 50 and 70 cm.

According to these results, the best track length for each pair (T, A) was also found, as presented in Fig. 6.24. Surprisingly, it does not differ significantly from the best track length in terms of final velocity, except for the pairs (3000 ms, 5°), (3000 ms, 15°) and (2500 ms, 45°). It appears the effect of more waiting time between peaks (longer periods) is

the same for all track lengths, so that, overall, the best track length for each pair (T, A) remains unaffected.

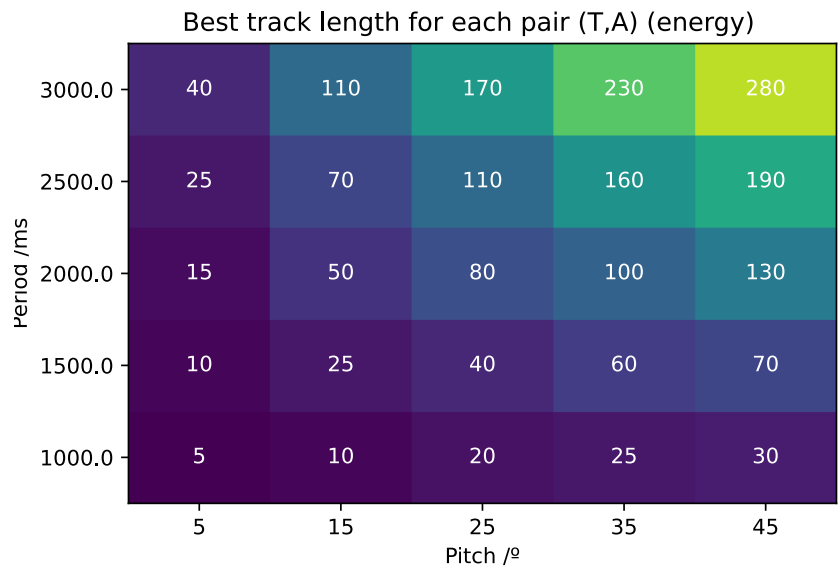


FIGURE 6.24: Best track lengths for each pair (T, A) in terms of total energy.

Chapter 7

Conclusions and outlooks

From materials selection, fabrication and characterization, to a specific device output evaluation and finally simulation of its operation, this work brought together different approaches for the same goal: optimizing the output of triboelectric nanogenerators.

We were able to fabricate uniform PTFE thin films and incorporate them in a TENG, generating power $\sim \mu\text{W}$. However, many difficulties and unexpected behaviors were encountered. It will be important, on a next step, to acquire or modify the substrates beyond mechanical pressing, to guarantee that their surface does not possess any significant curvature at the micrometric level; to deposit the PTFE film on rough substrates with similar average roughness, studying how that could be achieved beforehand; and in general, to optimize each parameter under study separately. A detailed annealing temperature study will provide information on the nanometric structures the PTFE coating develops and the crystallinity of the film, through SEM imaging, Raman spectroscopy to confront with FTIR results and X-ray diffraction before and after the annealing. Moreover, SEM imaging can be used to measure the thickness at the center of each sample (despite breaking it to obtain a cross section view), to build a thickness calibration with more spin speed values and statistics (several samples fabricated with the same spin speed), for the used PTFE solution deposited with spin coating.

As for the conditions of TENGs output measurement with the pneumatic motor, as referred it would be important to increase the frequency of the contact/separation cycle. However, this would more rapidly deplete the compressed air tank, reducing the measurement time in between compressions. Hence, the use of an electric and programmable linear motor can be a future upgrade of the system. Similarly, a leakage preventive version of the PCB Commutator needs to be developed for future use if automated output

for high impedances are to be measured.

The main objective this work was to relate the motion the UL-TENG is subjected to when inside a buoy to its electrical output. This comprised the evaluation of current and voltage peak shapes, internal resistance characterization and the multi-parametric study of the UL-TENG in track length, period and pitch amplitude of motion. The simulations provided valuable insight on the understanding of the experimental results. First, the peak shapes of current and voltage were better understood at the light of the COMSOL Multiphysics® simulation, that provided a correspondence between the position of the layers and the evolution of a current/voltage peak. Future steps can start by exploring why the open circuit voltage values analytically predicted and obtained with the capacitive model were different. Second, the origin of the deviation of the optimum resistance observed experimentally for different combinations of period and amplitude was found to be due to the closing/opening velocity of the generator in the simulations. Third, the closing/opening velocity proved to be a crucial parameter on maximum power. This supports the fact that the dependence of power (experimental) on period and amplitude can be explained by the very similar impact velocity of the sphere (simulation) dependence on those parameters.

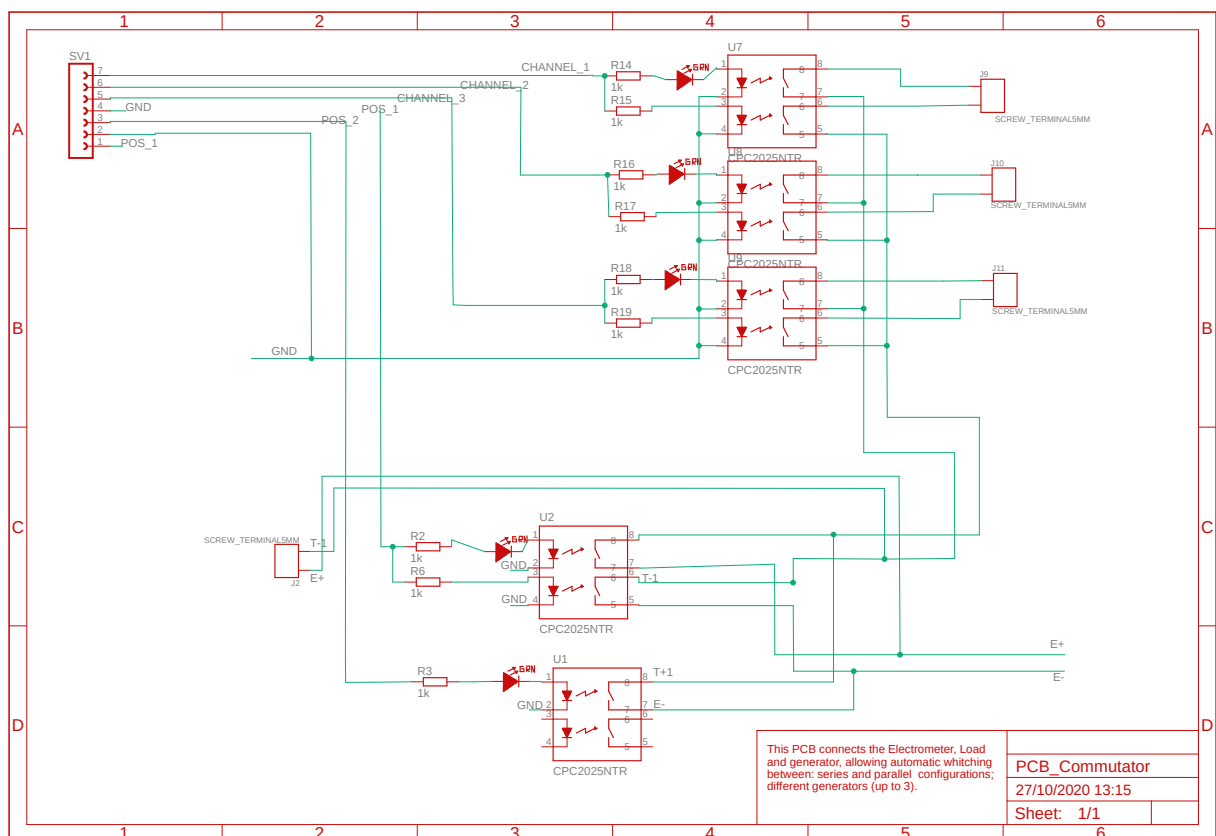
The 2-fold increase in output for the coupled UL-TENG, allied with the inclusion of more than one sphere (causing a more efficient charging and larger closing/opening velocity) define what could be the best UL-TENG overall. Nonetheless, future implementations should look after the optimization of the number of spheres. Including longitudinal gutters where the spheres would roll can also be beneficial, forcing an 1-axis rolling and preventing collision between spheres if several are included.

As for the initial question “Can the velocity of the rolling spheres be the linking parameter between the dynamics and the output of the UL-TENG?”, all findings point to a positive answer. Before this work, there was no clear relation between a rolling sphere velocity - dependent on buoy dynamics - and the power generated by the TENG it contacted/separated. It only remains to be experimentally investigated whether the total energy transferred to a particular device is related to the calculated total energy for each period and pitch. Nonetheless, from now on, new optimized TENGs can be designed with the best track length for a particular sea state, or combine several TENGs, with different track lengths, to increase the range of optimized harvesting in the period and pitch space.

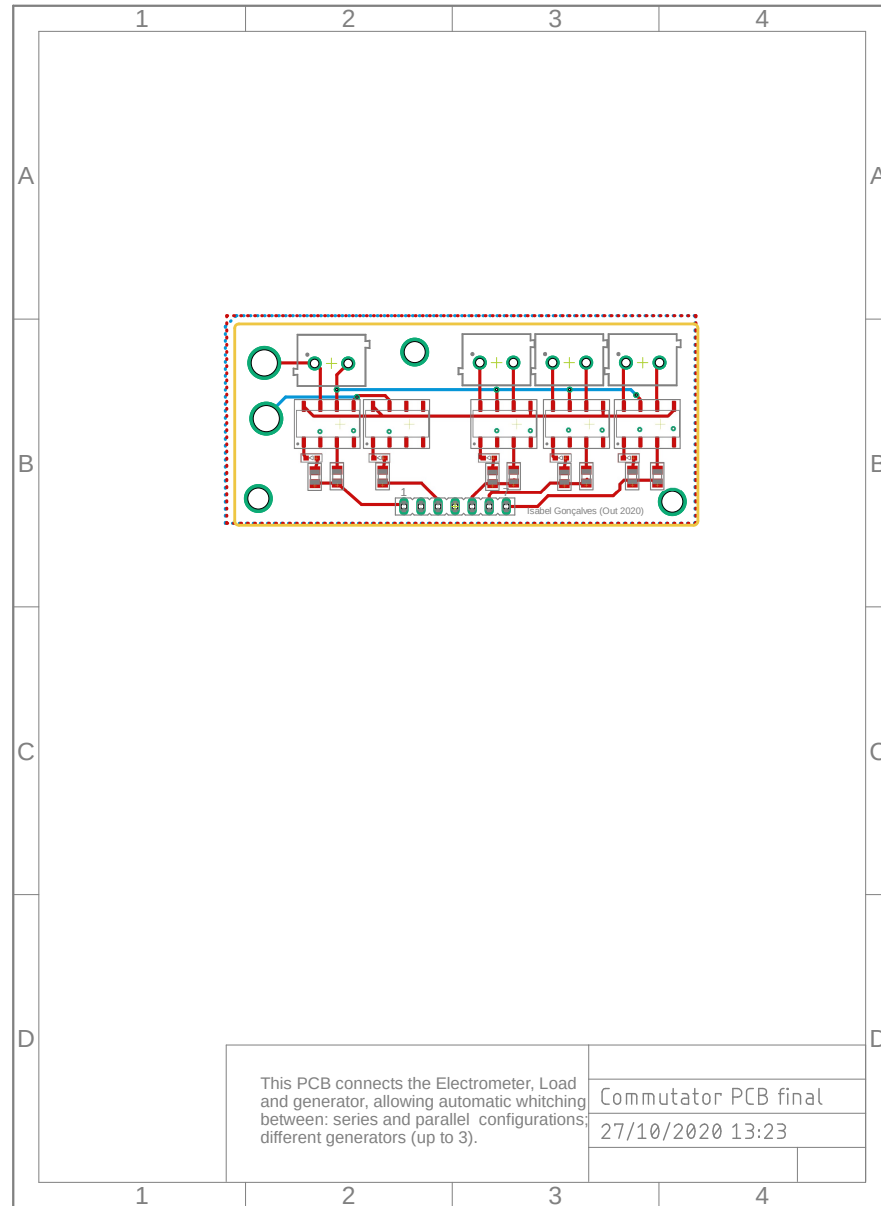
Appendix A

Schematics of PCBs

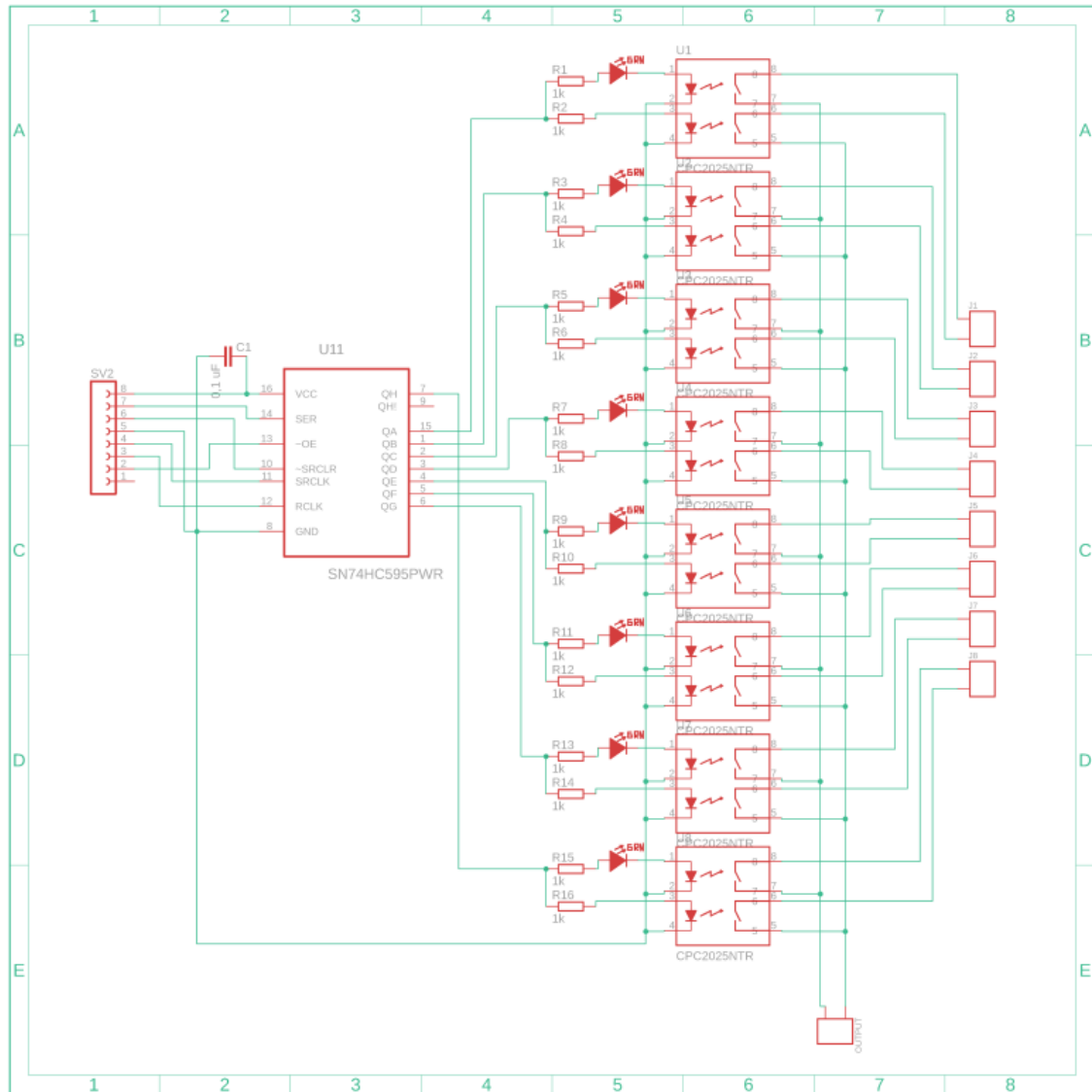
A.1 PCB Commutator - Schematic



A.2 PCB Commutator - Board



A.3 Box of resistances schematic



Appendix B

Acquisition and Motion System for TENGs Manual

Acquisition System for TENGs

MANUAL

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iNanoEnergy

Abstract

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1 System overview

This system creates a periodic movement for the TENGs, imposes the desired load or does a sweep of all the available resistances, acquires the voltage and/or current (sequentially) of each one (sequentially), and saves them into .txt format, as a function of time. It was created so that a single researcher could measure up to 3 TENGs, voltage and current, sweeping an array of periods and amplitudes that he/she wants, and sweeping all the resistances available as well, without ANY intervention. Everything is chosen beforehand, so after clicking “Run”, you are free to engage on another task.

It all starts with the mechanical parts: the servo motor has a configurable period and amplitude, and can be stopped and those parameters changed while the acquisition is running.

What controls the servo is the Arduino 1: it knows when to stop it, re-start it, change the period or amplitude. This Arduino also supports another task, controlling the Commutator, doing the switching between series connection (for current) and parallel connection (for voltage) automatically, while the acquisition is running.

Yes, there are two Arduinos: but one is hidden inside the box of resistances. Since it was first introduced in the system, it is called Arduino 2 in this manual. This box has a set of discrete resistances that can be chosen to represent the external circuit that each TENG sees. Being the first “feature” of the system, it communicates directly with the brain, the Mastermind: the Labview program.

“While the acquisition is running” refers to the running time of Labview. All those changes mentioned are done automatically by the program, therefore they need to be prescribed INITIALLY by the researcher. The Labview program is the user interface, where you must choose everything you want to do. It also includes a lot of Stop buttons if some mistake was done or anything odd occurred, so that you can start again with no problems.

Attention: At the present moment, the sweep is either on period and amplitude or in resistance, in order to study the influence of either the movement or the load on the TENGs’ electrical output.

2 Connections diagram

In the next page follows a complete diagram of the system, with all the needed connections.

Grounds: The GNDs of the Commutator, power supply and Arduino 1 are connected. The GND of the Electrometer isn’t the same, since it relates to the actual electrical circuit, with the TENG and load. The Box of resistances is only connected to the computer, so the GND for Arduino 2 is provided by the USB port. (Actually, the same happens for the GPIB communication between the electrometer and the computer, but that communication doesn’t affect the other GNDs referred).

OBS: Don’t place the Arduino 1 or Commutator (or any other PCB) over a metallic surface (for example, the mechanical system support). There may be conduction through that surface between the pins on the back of the board. You can use a simple sheet of paper as insulator and place it under the Arduino 1 and the Commutator.

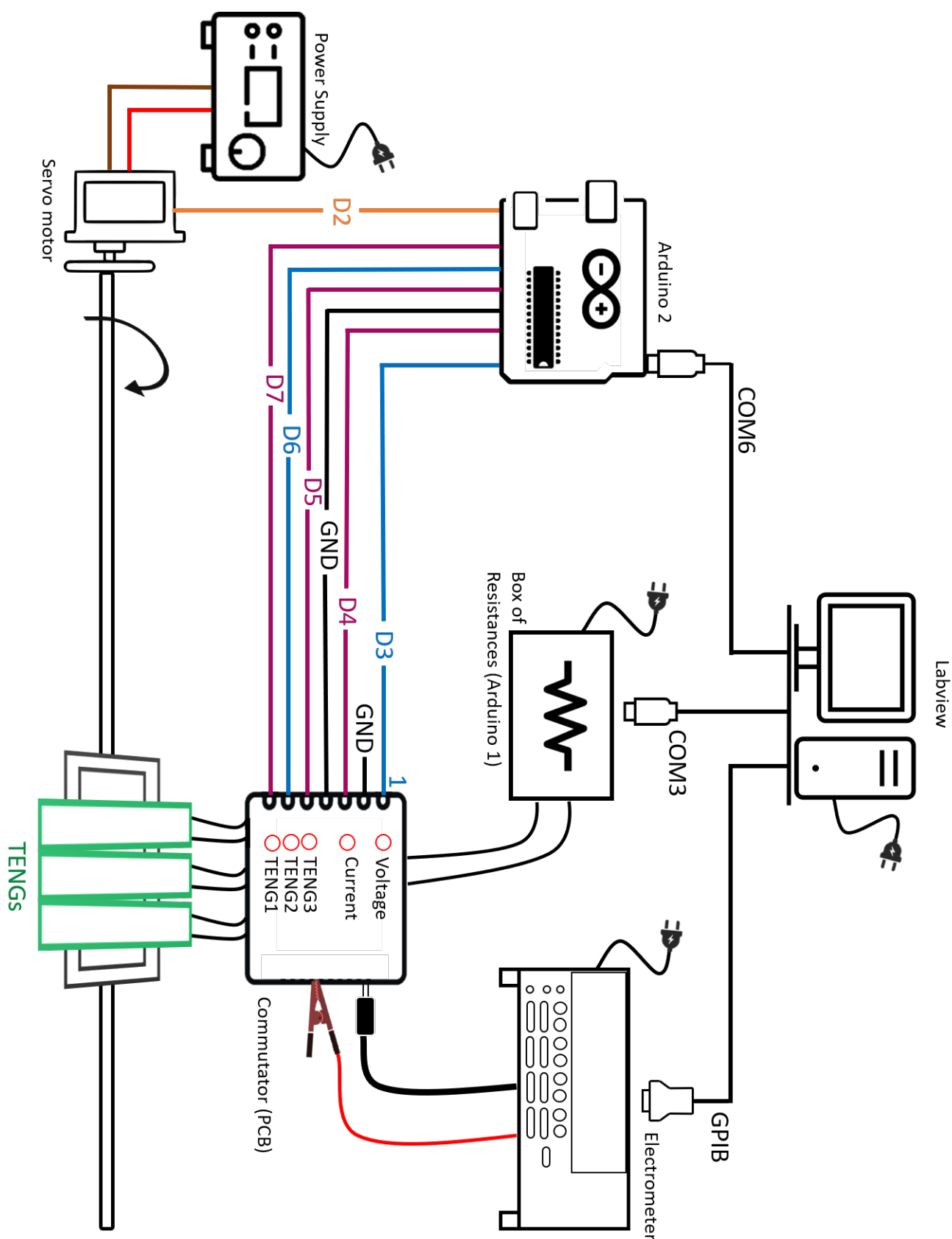


Figure 1: Diagram of the system's connections. In magenta and blue are the connections between the Commutator (starting in the female connector number 1) and the Arduino 1, labeled with its digital pin numbers (D3-D7). The Commutator doesn't have connections on all four sides, the Box of Resistances (Arduino 2) and the TENGs are connected on the same side in reality. For a complement to this diagram, check the beginning of the next section for a full list of components.

3 Components

This section includes a detailed description of each component in terms of Function(s), Inputs, Outputs, Working and Schematics/Figures to illustrate the connections. Some observations/warnings are included when necessary.

1. Labview program *Automatic Acquisition System*;
2. Arduino 1;
3. Commutator (PCB “Isabel Gonçalves Out 2020”);
4. Box of resistances (Arduino 2);
5. Electrometer (Keithley 6514);
6. Power supply;
7. Mechanical system with servo motor.

3.1 Labview program *Automatic Acquisition System*

This program is the user-interface and controls all other components, directly or indirectly, as well as receives data from the electrometer and saves it in .txt format.

Functions:

- Collect all the instructions from the researcher;
- Establishes the connection between the COM ports managed by Windows drivers and the user instructions;
- Controls everything in the electrometer through a GPIB port, from ranges to specific operating modes;
- Controls the duration of each measurement, operating over the electrometer, Arduino 1 and Box of resistances (Arduino 2) in specific moments in time;
- Sends Arduino 1 an instruction at the beginning of runtime and at each jump to another pair (*TENG, mode*) (the modes correspond to measuring voltage or current);
- Controls directly the resistance relays of the Box of resistances each time that is needed;
- Saves the data the electrometer outputs on the PC disk.

Inputs: GPIB cable from the electrometer;

Outputs: GPIB cable from the electrometer; Box of resistances (Arduino 2) USB port; Arduino 1 USB port.

Working: Front panel

Select your TENG(s): is the first panel, where the user can choose between measuring *TENG1*, *TENG2*, *TENG3* or *All*. If *All* is selected, the 3 TENGs will be measured sequentially according to the remaining settings. **If you choose All, the order 1-2-3 will be followed.** In the indicator *#TENG*, the number of the TENG that is being measured is shown (1, 2 or 3), that must coincide at all times with the turned on LED on the Commutator (for detailed information, refer to [Commutator \(PCB\)](#)).

The second panel is linked to the Acquisition Type (s) and measuring ranges, information that is given to the Electrometer and is represented in Figure 3. Intitulated *For each TENG*., you must choose the Acquisition Type between *Current*, *Voltage* or *Both*. **If you choose Both, voltage will be measured first.** On the indicator *Acquiring*., it will be displayed during runtime if the Labview is acquiring voltage or current, information that must coincide with the turned on LED on the Commutator (for detailed information, refer to [Commutator \(PCB\)](#)). In the *Voltage Range*, you can choose between the maximum values of [2V, 20V, 200V], range that will be constant throughout all resistances/pairs of period and amplitude. For measuring the direct output of a TENG, it is recommended to maintain this option at 200V.

On the other hand, the *Current Range* is defined for the first 7 resistances, for the two kind of studies (Resistance and P&A), while the *Current Range High R* is defined for the last 4 resistance values (10M Ω , 68M Ω , 100M Ω and 470M Ω), changing automatically during run time according to the resistance that is being measured. The available values are [20pA, 200pA, 2nA, 20nA, 200nA, 2uA, 20uA 200uA, 2mA and 20mA]. The value chosen *Current Range High R* must be equal or lower to the value chosen for *Current Range* and must be adapted to the output characteristics of each TENG. **Start with a high range to understand what are the maximum current values of your TENG and then reduce the ranges to obtain more accurate results.**

The third panel provides the options regarding each study, as can be seen in Figure 4. First, you must choose between the two available studies, *Resistance* or *P&A*. If you are interested on the resistance study, then you proceed to the section *Further resistance setup*, as you don't need to change anything on the field *Number of tests*. There, if you want to do a sweep

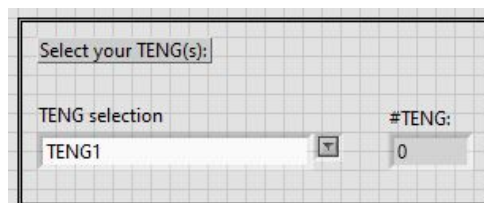


Figure 2: First section *Select your TENG(s)*: of the Labview's main program front panel.

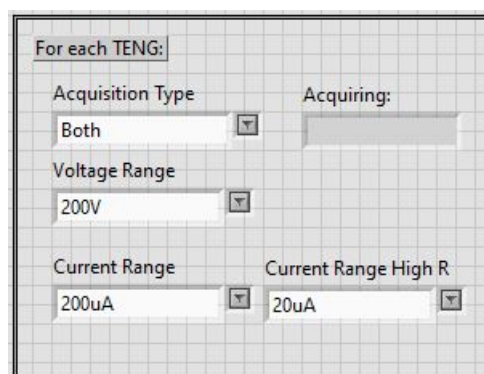


Figure 3: Second section *For each TENG*: of the front panel, relative to the electrometer parameters.

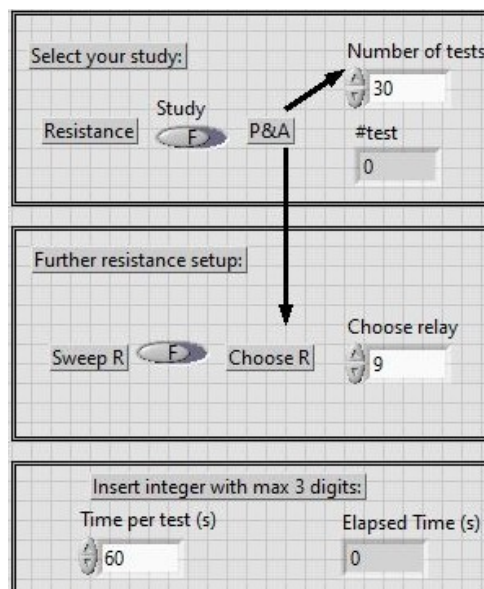


Figure 4: Third section of the Labview's main program front panel, relative to the intended study (Resistance or P&A).

of the 11 resistances, ignore the field *Choose relay* and proceed to finally choose the *Time per test* (s) (one test corresponds to one measurement, with one resistance). Contrarily, if you want to do a measurement with only one resistance, slide the button to *Choose R* and insert the corresponding relay index, consulting the table either on the Labview front panel or in this manual's section [Box of resistances \(Arduino 2\)](#). However, if you need to do a P&A study, click the sliding button on *Select your study*: and follow the arrows to necessarily insert the *Number of tests*, slide the second button to *Choose R* (since the resistance sweep isn't available on this study) and the *Time per test* (s) as well. These choices are summed up on Table 1. **OBS:** If you want to measure N periods and M amplitudes, then *Number of tests* will take the value $N \times M$.

Study	Number of tests	Choose Relay	Time per test (s)
Resistance + Sweep R	Indifferent (11)	Indifferent	Insert the desired value
Resistance + Choose R	Indifferent (1)	Insert the desired value	Insert the desired value
P&A	Insert the desired value	Insert the desired value	Insert the desired value

Table 1: Table of the fields available on the third panel. Marked in bold are the fields you must modify for each study.

The fourth panel is in Figure 5, where you must select the GPIB port where the electrometer is connected, and the COM ports of each Arduino. The default ports are already selected, but you must be sure the Labview is recognizing them, checking if their appear as an option in each drop down menu, clicking *Refresh* and un-connecting and connecting them again as needed. Shutting down Labview to remove the USB cables and connect them again may be needed as well. If the COM ports change, you can consult the Device Manager on the computer and NI Max interface to check their new designations. Ultimately, an indicator shows at the beginning of runtime the string sent to Arduino 1 that comprises the informations given in the first four panels, already described in this section. This string has the following format: *TENG/Acquisition Type/Number of tests/Time per test*, and some examples are presented in Table 2. The values for each of these segments are general instructions for the sequence of tests, only sent once at

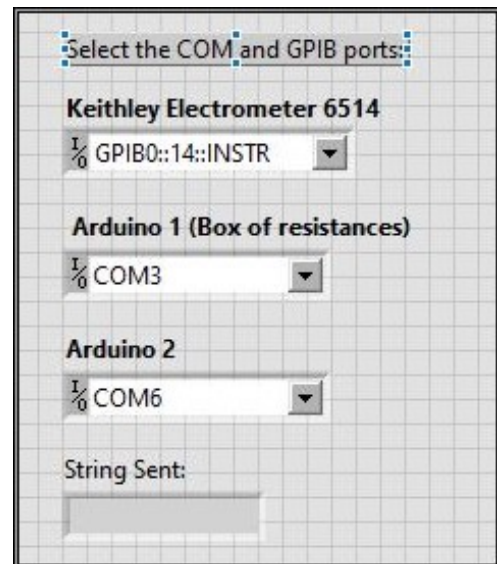


Figure 5: Section *Select the COM and GPIB ports*: of the Labview's main program front panel.

beginning of runtime, therefore aren't always the same as the displayed in the indicators on the precious panels. Their possible values are the following:

- TENG: 0 (All), 1 (TENG1), 2 (TENG2) or 3 (TENG3);
- Acquisition Type: 0 (voltage), 1 (current) or 2 (both);
- Number of tests: Number of 3 digits (max 999);
- Time per test: Number of 3 digits (max 999s).

Desired measurements	String
Measure current on TENG2 for 5 amplitudes and 5 periods, 60s each pair (P,A) (P&A study)	2/1/025/060
Measure all TENGs, both current and voltage, for 5 amplitudes and 5 periods, 60s each pair (P,A) (P&A study)	0/2/025/060
Measure all TENGs, both current and voltage, sweeping all resistances, 120s each one (Resistance study)	0/2/011/120
Measure all TENGs, both current and voltage, with only one resistance, for 120s (Resistance study)	0/2/001/120

Table 2: Example strings that the Labview routine will send to Arduino 1 according to the information provided by the user on the first four sections of the front panel.

On the next section of the front panel the base directory to save the acquired data is provided by the user. This directory is a folder, and the Labview program will create the needed folders and files inside it. A folder will be created for every TENG and for every Acquisition Type, as it can be seen in the examples given in the panel represented in Figure 6. According to the study selected, the filenames (format .txt) will be either the value of the resistance (resistance study) or the test number (P&A) study, starting in 0 (the .txt of the first test will therefore be called *0.txt*). **These folders and filenames were chosen to meet the requirements of the data analysis software and can be given to it as outputted by Labview.**

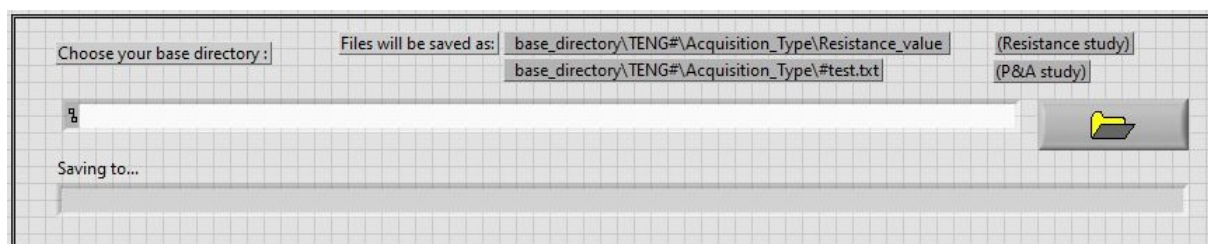


Figure 6: The section where the base directory is chosen, that presents also the generalized directory for each study.

In order to provide some examples, the previous table (Table 2) is recovered:

Desired measurements	Folders and Filenames
Measure current on TENG2 for 5 amplitudes and 5 periods, 60s each pair (P,A) (P&A study)	The files 0.txt, 1.txt, 2.txt (...) 24.txt will be created inside a folder named "Current" inside another named "TENG2"
Measure all TENGs, both current and voltage, for 5 amplitudes and 5 periods, 60s each pair (P,A) (P&A study)	Each of the folders "TENG1", "TENG2" and "TENG3" will have inside two folders, "Current" and "Voltage", and each of them will contain files named 0.txt, 1.txt, 2.txt (...) 24.txt
Measure all TENGs, both current and voltage, sweeping all resistances, 120s each one (Resistance study)	Each of the folders "TENG1", "TENG2" and "TENG3" will have inside two folders, "Current" and "Voltage", and each of them will contain files named 100.txt, 1000.txt, 10000.txt (...) 470000000.txt
Measure all TENGs, both current and voltage, with only one resistance, for 120s (Resistance study)	Each of the folders "TENG1", "TENG2" and "TENG3" will have inside two folders, "Current" and "Voltage", and each of them will contain one file whose name is the value of the chosen resistance

Table 3: Example folders and filenames that Labview will create according to all the settings.

The next section of the panel includes all the stop buttons. The Labview routine has a lot of cycles, therefore it needs all the four stop buttons. **ALWAYS use the stop buttons instead of the stop button of the whole Labview program, or you may encounter errors with the COM ports the next time you run it.** Make sure to follow the order of the buttons, and wait until the program stops, because it can take a few seconds. If the program doesn't stop anyway, and continues changing the resistance (you

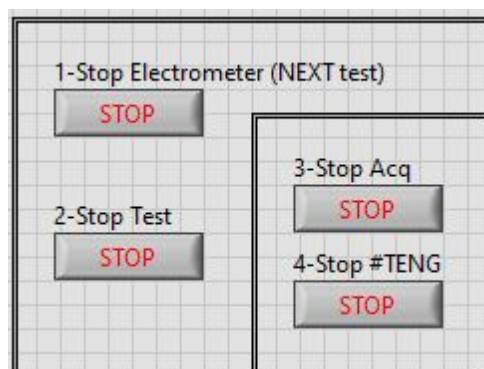


Figure 7: Section of stop buttons on the front panel.

will hear clicking sounds from the Box of Resistances), continue to click the stop buttons, even if out of order, until it stops. After the program has stopped, make sure to reset all the stop buttons to the unclicked position, so that when you run it again, they don't interfere with the measurements.

Important: Every time you stop the Labview routine, click the Reset button of the Arduino 1.

The panel includes some greyed indicators that display more specific information, as represented in Figure 8. The *Timing* is related to the electrometer measuring time, *Arduino 2 status* if the connection with the Box of Resistances (Arduino 2) was successful, and the *Measuring relay*: shows the index of the resistance that is being used, useful for the resistance sweep.



Figure 8: Some greyed indicators on the front panel.

Resistances											
100	1000	10000	100000	470000	1000000	4700000	10000000	68000000	100000000	470000000	
Relays Number											
2	3	4	5	6	7	8	9	10	11	12	

Figure 9: Table of resistances and their respective indexes for reference when choosing the desired measurement settings.

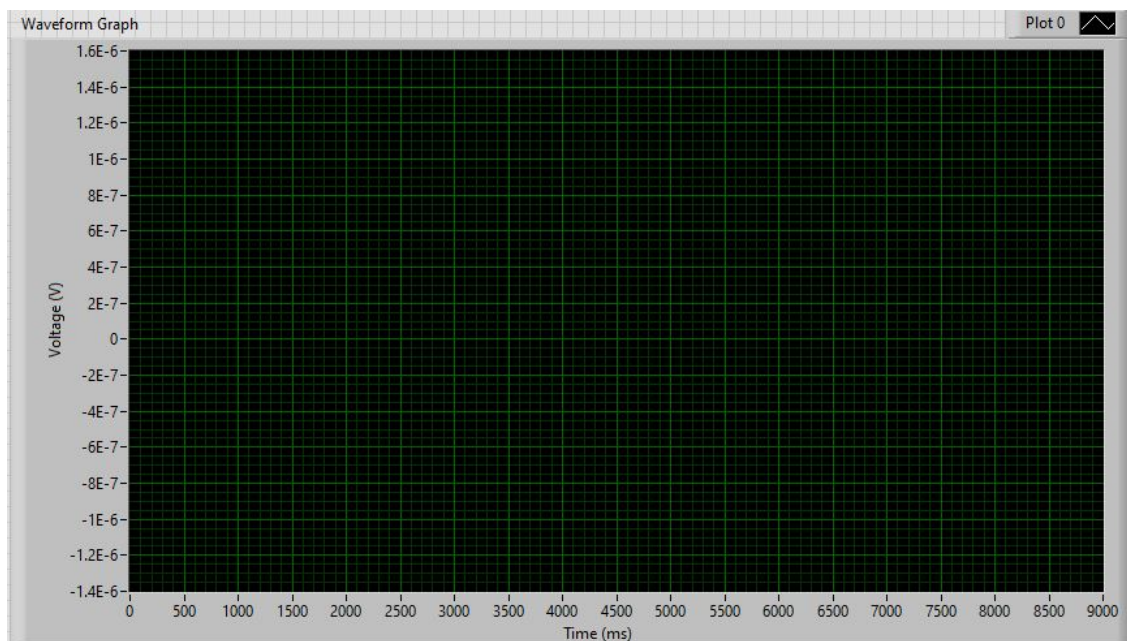


Figure 10: Graph where the voltage or current are plotted real time. The y-axis legend always stays as "Voltage", but it doesn't affect anything else.

3.2 Arduino 1

This component is the bridge between the Labview program and the mechanical system/Commutator: the hands and arms that perform what Labview commands. It receives information from the Labview program to execute a specific measurement or set of measurements, executing the prescribed “when” and “what”.

Functions:

- Directly controls the relays of the Commutator, controlling the voltage/current and TENG1, TENG2 or TENG3;
- Controls the servo motor, defining the period and amplitude of the frame’s periodic movement.

Inputs: USB cable from the computer. Serial data is received from Labview (string format).

Outputs: PWM to the servo motor on digital pin 2 (D2); Digital pins (D3-D7) (see Figure 11) to control the relays of the Commutator.

Working/code:

The first lines include the needed libraries; Then the servo object from the servo Arduino library is created; the “zero” for the servo motor is defined, in microseconds (user defined), corresponding to the position of the frame parallel to the table; and the slope m and intercept b ($y=mx+b$) of a linear calibration done to obtain the microseconds (y) from the frame angle measured from the horizontal (x); **If a sweep of Periods and Amplitudes is required, in this section you must insert the desired values in the two arrays “myPeriods” and “myAmplitudes”** as well as indicating the number of elements in each one. For example:

```
myPeriods[3] = { 1300, 1700, 2100 } ;
myAmplitudes[1] = { 30 } ;
```

The *setup()* function defines the state of the pins: all OUTPUT. It turns off the orange LED labelled with the letter L on the Arduino board, on the code called “LED_BUILTIN” . It attaches the pin D2 to the Arduino servo object, so that the library he knows where to output the PWM, and finally it puts the servo on position “zero” .

The function *OnePeriod(min_us, max_us, d_us, steps, Delay)* makes the servo motor execute one period, moving back and forth one time, according to the maximum position (maximum angle) value in microseconds (max_us), the minimum position (min_us), in a certain number of *steps*, with a *Delay* in milliseconds that was previously adjusted, being each two sequentially steps separated of an angle equivalent to d_us microseconds.

The function *execute_servos(Period, Amplitude, cycles)* executes the previous function for a fixed number of times given in *cycles*, making sure the desired *Period* and *Amplitude* is respected,



Figure 11: Picture of Arduino 1, where the digital pins are on the bottom right corner. Notice the reset button on the top right corner in red.

calculating the values *min_us* and *max_us* from those two input parameters. Here, *d_us* has the value of 10us, that was adjusted experimentally.

The *blinkk(times)* function blinks the built-in LED (labelled with letter L in the Arduino board), each second, the specified number of *times*.

The function *set_TENG(TENG)* imposes the value 1 or 0 in the D5-D7 pins, operating over the optical relays of the commutator responsible for choosing one TENG at a time: the selected TENG will have its correspondent relay receiving 1, the other receive zero.

The function *set_mode(mode)* imposes the value 1 or 0 in the D3-D4 pins, controlling the optical relays of the commutator to choose series or parallel connection. When one relay receives 0, the other must receive the value 1, and vice-versa, meaning that **when one switch is closed, the other must be open** in order to have a series or parallel connection and not a dangerous combination of the two.

The function *N_Test(N_measurements, dT_measurement)* executes the previous function *N_measurements* times, each time for *dT_measurement* seconds. **In this function, you need to comment some lines to change between using always the same Period and Amplitude to a sweep of Periods and Amplitudes, as well as inserting the desired Period and Amplitude in the first case. Refer to the [Quick starting guide](#) for more information.** Periods must be given in milliseconds and amplitudes in degrees. In a sweep, the system goes through all amplitudes for the first period before moving to the next period.

The *loop()* function is the main function in Arduino, it has the principal program that calls all the other functions, and as its name implies, is always running. The first thing this Arduino does is to set up the servo to the initial position, an useful instruction after the first loop, hence the first prescribed measurement, ends. One loop corresponds to the full acquisition program as commanded by Labview, therefore, when the Labview programs finishes, the servo motor stops the periodic movement and goes back to the initial position as prescribed on the beginning of the *loop()* function.

After connected, this Arduino waits in a while loop for a string of instructions given by Labview, blinking the control LED (labelled with letter L in the Arduino board). When it is received, the LED lights on permanently. It is crucial that the string is received, otherwise the electrometer will read wrong voltages/currents, since it won't be connected nor in series nor in parallel, and the servo won't move either.

The received string is parsed to provide the following parameters: *TENG*, *mode*, *N* and *dT*:

- *TENG* may take the values 0,1,2,3: from 1 to 3 indicates the number of the TENG that one desires to measure, and 0 indicates that the user wants to measure them all sequentially.
- *mode* takes value 0 if the intended is to measure only voltage, 1 for current, and 2 for both of them, sequentially.
- *N* and *dT* correspond to the number of tests and duration of each test, and are given as the parameters to the *N_test(N_measurements, dT_measurement)* function.

This string has the format TENG/mode/N/dT, being N and dT always a set of 3 digits/characters. For instance, if the user wants to measure the TENG number 2, both current and voltage, for 4 measurements (example 2 periods x 2 amplitudes), of 60 seconds each, the string sent from Labview

will be: 2/2/004/060. These values are actually read as integers thanks to the *strtok(data, separator)* and *atoi(index)* functions, ignoring the value of each ASCII character that composes the string.

The following section simply executes the user choices. The Arduino first checks if the user is interested in all TENGs, or only one, saving this information in the parameter *nTENG*, that corresponds to the number of TENGs to measure, either 1 or 3. If both modes, voltage and current, are required, it proceeds to check the TENGs. If *nTENG* = 1, the value saved in the TENG parameter is always greater or equal to count, that starts with the value of 1, its value (1, 2 or 3) prevails on the operation *max(count, TENG)*, and therefore the desired TENG is selected in *set_TENG(TENG)*. If *nTENG* = 3, *TENG* had the value of 0 from the received string, hence the variable *count* will always be greater, executing the sweep of the TENGs in the order TENG1 – TENG2 – TENG3 in the first *for* loop: So, if all TENGs are required, **it starts with TENG1**. The mode is then selected, **choosing voltage first** on the function *set_mode(mode)*, then measuring current, for the same TENG, before advancing to the next TENG. In order to proceed from one pair of (*TENG*, *mode*) to another, the Arduino waits for a Serial message from the Labview program. This ensures the synchronization between the two.

On the other hand, if only one mode is selected, it is immediately selected in *set_mode(mode)*, and the same reasoning for the selection of TENGs follows.

This arrangement allows for all combinations: measuring one TENG in both modes, measuring all TENGs in one mode, or the three TENGs in both modes.

3.3 Commutator (PCB)

This component is a panel of switches controlled by Arduino 1 code, in its turn controlled by the Labview program.

Functions:

- Chooses 1 of 3 TENGs that can be connected simultaneously;
- Chooses to measure voltage or current, changing the connections between the TENGs, the resistance box and the electrometer between series and parallel.

Inputs: Electrometer (desirable polarity in the figures); Box of resistances (no polarity); TENGs (no polarity); Arduino digital pins 3 to 7 (D3-D7) and GND (see Figure 11). OBS: These pins are 5V outputs from Arduino.

Outputs: None.

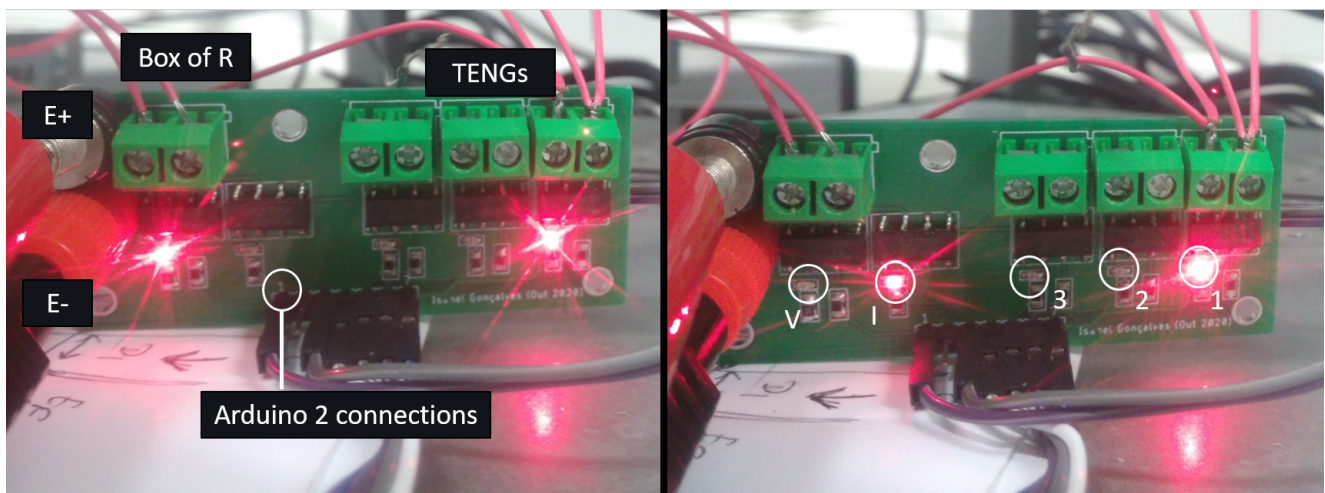


Figure 12: On the left, the connections with Arduino 1, where the pin number 1 is highlighted, TENGs, Box of Resistances and Electrometer (positive and negative terminal). On the right, the LEDs' meanings: The first light indicates the commutator is on the parallel state; the second in the series state. The third, fourth and fifth LEDs indicate which TENG is connected 3, 2 or 1, respectively. Both pictures have the TENG1 selected, but in the first it was being measured voltage, and on the second current.

Working: The Arduino code controls directly the switches (optical relays) in the Commutator. It has 2 switches (optical relays) to control the measurement in series/parallel and 3 switches (optical relays) to choose the TENGs. Each relay is controlled by an Arduino pin. The switches close if they receive a digital signal of 1 and open if they receive a digital signal of 0 from the corresponding Arduino pin. At each measurement, there must be always two lights on: one that indicates the connected TENG and another that indicates if the electrometer is connected in parallel or in series, see Figures 12 and 13.

In Figure 13 is represented the internal circuit respecting to the commutation voltage/current. When B and C are closed, A must be open, and the commutator is on parallel state. When A is closed and B and C open, the commutator changes to the series state. Since two of the switches have always the same state, only 2 optical relays were needed.

3.4 Box of resistances (Arduino 2)

This component imposes a resistance on its terminals, chosen by the Arduino 2, built-in in the box, in its turn controlled by the Labview program.

Function: Imposes a purely resistive load on its terminals: [100, 1k, 10k, 100k, 470k, 1M, 4.7M, 10M, 68M, 100M, 470M] Ω .

Inputs: 12V, 1.5A from a charger; Micro USB from the computer to receive instructions from Labview.

Outputs: None.

Working: The built-in Arduino 2 controls the mechanical switches to connect to the box's terminals the desired resistance. Each mechanical

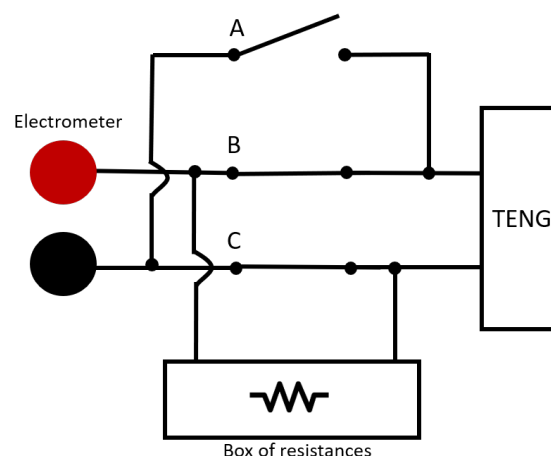


Figure 13: Internal switches that control the parallel/series state. On the box *TENG* is connected the other part of the circuit, that pays respect to the switching between TENGs.

relay is controlled by a digital arduino pin (D2-D12) as expressed in the table 4.

Relay #	2	3	4	5	6	7	8	9	10	11	12
Resistance / Ω	100	1k	10k	100k	470k	1M	4.7M	10M	68M	100M	470M

Table 4: Correspondence between resistances and the digital pins of Arduino 2.

OBS: When properly connected, the user will hear a clicking sound. When the resistance is selected by the Labview, another sound will be heard, corresponding to the switching of the mechanical relays.

OBS 2: You can connect any external circuit in these terminals apart from the box of resistances, or even a circuit that includes it. Nonetheless, keep in mind that the electrometer's terminals in the Commutator won't change, corresponding always to the same two nodes in the circuit, the ones where you connect your custom external circuit. On another words, you may need to change the electrometer's terminals to another part of your circuit in order to measure voltage or current in the site of interest in your circuit. In that case, the functionality of measuring in series or parallel will influence your results, therefore you will need to manually change the electrometer's terminals: refer to the schematics of the Commutator to make the necessary changes in the connections.

3.5 Electrometer (Keithley 6514)

This component acts as voltmeter and ammeter.

Functions:

- Measures voltage and current with high acquisition rate;
- Transmits that data to Labview.

Inputs: Labview commands through GPIB port.

Outputs: Data through the GPIB port to Labview.

Characteristics: Acquisition rate: The Electrometer's integration time can be set to be 0.01 - 10 times the period of the grid or power line cycles (PLCs). In this system it is programmed to the fastest integration possible, $0.01/50\text{Hz} = 0.2\text{ms}$. The acquisition rate depends on this value and according to the datasheet is equal to 1200 measurements/second, hence an acquisition time for each point of 0.833ms.

Terminals: The positive terminal is the red crocodile on the tri-axial cable, while the negative terminal (for GUARD mode) is the COMMON on the back of the device.



Figure 14: Box of Resistances with built-in Arduino, labeled.

In order to prevent significant errors in the measurements due to current leakages when measuring high impedances, the electrometer must be used in the Guard Mode (configured by GPIB code). Additionally, shielded cables should be used as connecting wires from the TENG to the electrometer and the cables should be inside a Faraday cage (at least the naked crocodiles or other conductors).

For more information read the [Keithley 6514 Electrometer manual](#) (link available at Feb 2021).

Working: The Labview sends GPIB code to the Electrometer to control the mode of operation (voltage /current), each range, and set the Guard Mode on. The electrometer performs a certain number of measurements, being the maximum 2500, before storing them to a buffer and sending them to Labview. This results in data being sent from 2.932 to 2.932 s to Labview (moment in which the graph is also updated) and the electrometer losing 340 ms of data in the process. The time values registered in the .txt files are not provided by the electrometer, but calculated on Labview as 2.932 s / 2500 points.

3.6 Power supply

This component provides a 7.4V and 3A (stall current of the servo motor) power to the servo motor.

OBS: Use a good power supply, isolated from the noise in the electric grid, otherwise, that noise will be captured through the connected GNDs and interfere with the measurements made (even though the electrometer GND isn't connected to the power supply GND).

3.7 Mechanical system with servo motor

This component is responsible for holding the TENGs and communicating the movement imposed by Arduino 1 on the servo motor to the TENGs.

Functions:

- Provides support to the TENGs, possessing a rotating frame where they are fixed (usually glued and attached with ribbons, although holes for screwing exist).
- Transmit movement from the servo motor DF15RMG to the frame.

Inputs: Power supply to the servo motor; PWM pin from the Arduino 1.

Outputs: Movement only.

Working: The rotating axis of the motor is connected to the axis of the frame not through a belt but with a rigid piece and a screw. The screw is fixed on a disk centered on the axis of the frame that rotates along with it.

OBS: With time, the screw can degrade the main axis disk, therefore maintenance may be needed. If you notice little jumps in the frame movement, it may be a sign of a damaged screw hole.

4 Calibration

If you notice that for some reason the period or amplitude you want isn't being respected, you can calibrate the system. To calibrate amplitude: Go to Arduino 1 and set up the servo motor to defined values in microseconds (in the range $[530 - 2400]\mu s$), measure the angle the frame does with the horizontal for each one (suggestion: taking a picture and measuring the angle with a program, for

instance, ImageJ), and calculate a linear fit $y = mx + b$ angle(microseconds). Insert the obtained fitting parameters m, b in the first lines of Arduino 1 code.

To calibrate the period: Go to the function `execute_servos(Period, Amplitude, cycles)` and find the variable *factor*. Adjust its value until you measure the desired period, on the range of periods you need.

5 Quick starting guide

Always turn on the Electrometer first, at least 1 hour before starting data acquisition: its measuring error decreases with time.

5.1 Resistance study

1. Open the Arduino 1 code and search for the function `N_test(N_measurements, dT_measurements)`;
2. Find the comment that says: *Insert the values below to do a resistance study (=> you only need one (P,A) pair)* and proceed to insert the desired amplitude and period of the movement;
3. Find the two comments *Comment the block loop below to do a resistance study (=> you only need one (P,A) pair)* and proceed to comment each block until its respective asterisk line;
4. Upload the code to the Arduino 1 and make sure to connect it in the PC that will execute the main Labview program;
5. Connect everything as in the [Connections Diagram](#) and open Labview *Automatic Acquisition System*;
6. Make the selections you desire in the panels *Select your TENG(s)*, *For each TENG:*, *Select the COM and GPIB ports:* and *Choose your base directory*. For detailed information on these panels visit the section [Labview program Automatic Acquisition System](#);
7. On the panel *Choose study:*, click the sliding button to the side that reads *Resistance*;
8. You can choose to acquire data with only one resistance (*Choose R*) and write correspondent relay index in *Choose relay* or to do a sweep of resistances (*Sweep R*), in the sliding button of the panel *Further resistance setup*;
9. You don't need to insert the number of tests, any value on that field will be disregarded, since it is inserted automatically in the code;
10. Insert the duration of each test in seconds (max 999 s). In this study, it corresponds to the time of the measurement for each resistance, either if you chose only one or several;
11. Run the Labview program.

5.2 Period and Amplitude (P&A) study

1. Open the Arduino 1 code and in the first lines find the comment *Insert the values below for a period and amplitude (P&A) study*;
2. Create two arrays, one called *myPeriods* and another *myAmplitudes* with the number of *N* and *M* number of elements, respectively (for detailed information on how to create arrays go to [Arduino 1](#));
3. Search for the function `N_test(N_measurements, dT_measurements)` and comment the block under *Insert the values below to do a resistance study (=> you only need one (P,A) pair)*;

4. Make sure the blocks *Comment the block loop below to do a resistance study* ($\Rightarrow$ you only need one (P,A) pair) (there are 2) are uncommented;
5. Upload the code to the Arduino 1 and make sure to connect it in the PC that will execute the main Labview program;
6. Connect everything as in the [Connections Diagram](#) and open Labview program *Automatic Acquisition System*;
7. Make the selections you desire in the panels *Select your TENG(s)*, *For each TENG*:, *Select the COM and GPIB ports*: and *Choose your base directory*. For detailed information on these panels visit the section [Labview program Automatic Acquisition System](#);
8. On the panel *Choose study*:, click the sliding button to the side that reads *P&A*;
9. You can only acquire data with one resistance, therefore you must click the sliding button on the panel *Further resistance setup* to read (*Choose R*);
10. Write correspondent relay index in *Choose relay*;
11. Insert the number of tests, that equals $N \times M$;
12. Insert the duration of each test in seconds (max 999 s). In this study, it corresponds to the time of the measurement for each pair of amplitude and period, either if you chose only one or several.
13. Run the Labview program.

Stop buttons: PRIORITIZE THE STOP BUTTONS over the stop on Labview. Follow the order 1-2-3-4.

You can change the Arduino code with the labview open, if you always used the stop buttons.

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