Energy Harvesting Using PVDF Piezoelectric Nanofabric

By

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A thesis submitted in conformity with the requirements for the degree of Masters of Applied Science in Mechanical Engineering
Mechanical and Industrial Engineering
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Abstract

Energy harvesting using piezoelectric nanomaterial provides an opportunity for advancement towards self-powered electronics. The fabrication complexities and limited power output of these nano/micro generators have hindered these advancements thus far. This thesis presents a fabrication technique with electrospinning using a grounded cylinder as the collector. This method addresses the difficulties with the production and scalability of the nanogenerators. The non-aligned nanofibers are woven into a textile form onto the cylindrical drum that can be easily removed. The electrical poling and mechanical stretching induced by the electric field and the drum rotation increase the concentration of the piezoelectric β phase in the PVDF nanofabric. The nanofabric is placed between two layers of polyethylene terephthalate (PET) that have interdigitated electrodes painted on them with silver paint. Applying continuous load onto the flexible PVDF nanofabric at 35Hz produces a peak voltage of 320 mV and maximum power of 2200 $\frac{\text{W}}{\text{cm}^2}$.
I would like to sincerely thank Professor Ridha Ben Mrad for his providing me with his time and guidance throughout the process. I feel very fortunate to have had a thesis supervisor that supported my ideas and took an active interest in this project.

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Chapter 1

1 INTRODUCTION

1.1 Problem Statement

Energy harvesting describes generating, capturing and storing of energy for self-powering handheld devices. The energy is derived from solar, wind, thermal and kinetic energy to power low energy devices. In some situations the devices rely on batteries for power and recent efforts have been made to introduce energy harvesters to complement the batteries for situations in which battery replacement is not possible. Nanogenerators are nano-sized energy generators that can both complement a battery or in some cases be standalone power providers for small electronic devices. Piezoelectric materials have been widely used as the primary element of many energy harvesters, mainly ceramics and in the bulk form. Recent studies into polymer and composite piezoelectric alternatives, in thin film and nanofiber forms, have led to the development of the recent nanogenerators and harvesters. The challenge faced by most researchers is fabricating piezoelectric nanogenerators that can provide enough power to operate handheld devices.

1.2 Objective

The objective of this project is to design, fabricate and test an energy harvester for the wearable electronics and sensors industry. Previously existing methods have laboratory and cleanroom fabrication environments. It is hard to scale such designs for mass production. In order for a nanogenerator to be used in wearable electronics, the proposed generator must be flexible, bio-safe and free of any hazardous materials. The objectives of this project in regards to the fabrication include: decision making on the materials used for the nanogenerator; the production of the material; and selecting a fabrication method. Once the nanogenerator is made, the sample needs to be tested using characterization tools to check for piezoelectricity. Finally, testing techniques need to be designed for the measurement of the power output.

The power output of the nanogenerator is the most significant objective. The power must be high enough to potentially power electronic devices and surpass the current highest power achieved, $577.6 \frac{\text{mW}}{\text{cm}^2}$, with polymer nanogenerators.
1.3 Chapter Outline

The thesis is presented in 4 chapters, representing the design, fabrication and experimental efforts of this project. This chapter will begin with an in depth review of fundamentals of electrospinning and move on towards a review of nanogenerators. This chapter will discuss fabrication methods of nanogenerators made from different materials including ceramics and polymers. Chapter one includes an introduction of characterization methods used in the subsequent chapters. The chapter will end with the contributions of this project. Chapter two demonstrates the experimental processes of material selection and the characterization methods used for validating any decisions made. The chapter continues with detailed descriptions on the electrospinning method used for the fabrication of the nanofabric and steps taken to optimize the process. In chapter three, different experimental settings are introduced for the testing of the nanofabric. This chapter includes the details of the experiments, measurements and the piezoelectric response validation. The final chapter describes the summary of the dissertation with recommendations on future works to further improve the performance of the nanofabric.

1.4 Background Review

This section includes an overview of methodologies, setups and materials used in the design and fabrication of piezoelectric nanogenerators. The fundamentals of electrospinning are introduced as the primary fabrication method of this report followed by a review of previous work on piezoelectric nanogenerators including those made of lead zirconate titanate (PZT), zinc oxide (ZnO) and PVDF.

1.4.1 Fundamentals of Electrospinning

Electrospinning is one of the most versatile fabrication and manufacturing methods for the production of nano and micro devices. By means of this method molten material can be turned into fibers with diameters ranging from tens of nanometers to a few micrometers. The range of “electrospinable” materials includes organic or synthetic polymers, polymer alloys, metals and ceramic materials [1]. Different electrospinning methods have been developed to fabricate hollow tubes and complex nanostructures used in biomedical [2] and tissue engineering applications, design of optical sensors [3] transistors [4] and filters. In a very interesting application Takahashi et al. [5] have worked on the use of electrospinning for the fabrication of
DNA nanofibers. Li et al. [6] [7] studied the electrospinning of more than fifty organic polymers, including biopolymers and degradable engineering plastics, for electro-optical applications. Huang et al. [8] have conducted a comprehensive review of polymer materials used in electrospinning for the fabrication of nanocomposite in medical and pharmaceutical applications. A recent review by Nayak et al. [9] considered many of the advancements in the field of electrospinning including multi-jet and needless electrospinning.

1.4.1.1 Principles of Electrospinning

A typical electrospinning setup will include a nozzle, high electric fields and a grounded collector. These three main elements need to be included in all of the complex electrospinning designs. A typical setup of electrospinning is shown in Figure 1 [10]. The process begins with the feeding of the solution through a nozzle using a mechanical pump with control over the flow rate. A high voltage source, typically in the kilovolts range, is used to create a critical electric field such that the solution starts to move towards the tip of the nozzle; the repulsive force within the charged solution is balanced by the surface tension of the solution. This balance results in the accumulation of the solution at the tip of the nozzle to create a droplet, called the Taylor cone. Once the electric charged force within the solution surpasses the surface tension force a jet discharges from the tip of the nozzle. As soon as the charged solution leaves the nozzle it rapidly becomes unstable and enters a bending instability stage. Yarin et al [11] studied the instability of the bending stage using polyethylene oxide (PEO) as the electrospinning solution, seen in Figure 2. Finally, a grounded collector is used to collect the produced fibers; this collector can be a static flat surface or any other complex setup such as a drum with patterned electrodes. Depending on the distance the solution has to travel before reaching the collector, electrospinning can be divided into two areas: near-field electrospinning, when the distance is very small; and far-field electrospinning, for when the collector is not placed immediately after the droplet.
1.4.1.2 Far-Field Electrospinning (FFES)

Most traditional electrospinning methods can be classified as far-field electrospinning. In this type of electrospinning the distance between the nozzle and the grounded collector is tens of centimeters. This long distance results in chaotic and somewhat uncontrollable jet paths travelled by the charged solution. During this process, the solvent evaporates and the polymer/composite fibers solidify to form randomly oriented nanofibers. The typical needle diameter is a few micrometers and the voltage applied ranges from 10 to 20 kilovolts. The electrostatic forces in the field cause the viscoelastic solution to stretch while being charged and poled by the electric forces.
field. The key challenge of far-field electrospinning is the random distribution of the nanofibers. Researchers have developed fabrication techniques to overcome the random orientation of the fibers by means of non-static collectors or introducing patterns onto the collectors. Boland et al. [12] proposed a method of controlling the electrospinning of poly glycolic acid using the rotation speed of the cylinder collecting drum, for applications in tissue engineering. The use of speed to control the fiber orientations and position has been used with drums [13], sharp edged thin drums [14] and wire drums [15]. Section 1.4.2.4.1 of this thesis will introduce new developments in the fabrication of aligned PVDF nanofibers using electrospinning. Figure 3 presents electrospinning using a wire drum collectors.

Figure 3. Copper wires used for the collection of the nylon nanofiber mat. Bottom right corner is a magnified view of the mat [15]

1.4.1.3 Near Field Electrospinning (NFES)

Near-field electrospinning (NFES) introduces a new method of electrospinning with superior control on the fiber diameter and orientation. This method calls for a dramatic reduction of the needle to collector distance, to less than one millimeter, and applied voltage, to less than 1 kV. This increased electric field (due to much shorter separation between needle and collector) makes it possible to perform the depositions while the liquid jet is still in the stable region [16]. In the earlier developments in the field of NFES, Sun et al. [17] proposed a “dipped pen” approach in which a tungsten electrode with a 25 µm diameter is used to fabricate a nanofiber with diameters ranging from 50-500 nm. The liquid supply to the probe tip is analogous to that of a dip pen. This method is presented in Figure 4 (a) and (b). Chang et al. [18] further developed
the NFES concept into continuous NFES by replacing the dip probe with a syringe so that the electrospinning solution is constantly available through the continuous supply in the syringe. This last method is comparable to the conventional far-field electrospinning in that it allows for the continuous fabrication of nanofibers with superior controllability on the deposition orientation and position, Figure 4 (c).

![Figure 4](image)

**Figure 4.** (a) Schematic demonstration of the NFES method using the tungsten electrode probe. [16](b) An optical image demonstrating NFES with dip-pen approach. [17] (c) An optical image demonstrating NFES with a syringe instead of probe to supply electrospinning solution [18]

### 1.4.2 Review of Nanogenerators

The rapid advancements in hand held devices over the years led to the need for battery supplements and potential replacements. The stand-alone devices require a constant source of power beyond the rechargeable batteries. In situations in which having batteries might be cumbersome, an alternative source of energy is compulsory. Harvesting energy from the environment has proven to be a great contender for self-powered energy sources. These types of environment-powered energy sources include solar energy [19], energy harvested from minor mechanical vibration [20] [21] and thermal energy.

The science of piezoelectricity and the recent developments in nanofabrication have the potential of bringing a fundamental solution to energy needed to drive hand held devices on self-powered energy sources. Compared to their bulk counterparts, nanofibers have a unique density of electronic states and so exhibits significantly different optical, electrical and magnetic properties
The advantage of using nanofibers for energy harvesting is their high mechanical robustness and responsiveness to small mechanical disturbances [23]. The ZnO nanogenerator developed by Wang et al. [24] was one of the early signs of the potential of piezoelectric nanofibers [25]. The fabrication method used was still far from mass production of nanofibers but a great breakthrough in the experimental analysis of the nanofibers.

Extensive research has been done on the different methods of energy harvesting using nanogenerators, considering the use of different materials and structures. The designs include mat/surface-based nanostructures, nanofiber based generators and electrospun nanogenerators. The film/mat-based nanogenerators are deposited or printed nanofibers on drums or thin films. These include piezoelectric ribbons printed from thin films onto flexible substrates [26], piezoelectric fiber composites [23], integrating piezoelectric ZnO nanofibers and a charged dielectric film on wearable textile substrate [27] and sputtering ferroelectrics on flexible substrates [28]. The nanofiber based generators [29] are often developed using semiconductor materials which generate power by being strained with the tip of an Atomic Force Microscope (AFM) [24] or the use of zigzag electrode structures [30]. These semiconductors include ZnO [24] [31] [32], zinc sulfide (ZnS) [33], gallium nitride (GaN) [34] [35] or cadmium sulfide (CdS) [36] [37]. The final categories of structures are the electrospun nanofibers. The materials used for fabrications using electrospinning vary, but the most common and interesting ones are ZnO [38], PZT [39] and PVDF [40]. This technique has been explored for many years now and has led to successful production of various organic, inorganic and composite nanofibers [41] [42] [43]. Many efforts have been put on designing nanodevices using the electrospun nanofibers [44] [45].

ZnO exhibits both semiconducting and piezoelectric properties that form the basis of the electromechanically coupled sensors and transducers [24]. The coupling of ZnO’s piezoelectric and semiconducting properties is the key to power generation using piezoelectric nanofibers [46] [47]. ZnO has demonstrated to be bio-safe and biocompatible with little toxicity [48]. Finally ZnO demonstrates the most diverse configurations ranging from nanofibers [49], nanobelts [50], nanosprings [51] and nanoheleices [52].

PZT is a ceramic piezoelectric material and is probably one of the most important piezoelectric owing to its remarkable piezoelectric performance [53]. The existence of directional behavior for the dielectric and piezoelectric performance of PZT has been studied by Du et al. [54]. PZT has
an asymmetric crystal structure and its reaction towards an applied electrical field is the fluctuating, up or down, of the Zr/Tr atom. PZT provides fast response to applied voltage and has very large piezoelectric constant values [55] [56] compared to other nanofibers [57] (depending on production method as discussed later). The primary downside of using PZT is that it contains lead and lead is known to adversely influence the human organisms [58]. The fabrication of PZT thin films and microfibers usually requires high temperatures (~650 °C) [59] to increase the crystallinity, which leads not only to high cost and incompatibility with general fabrication processes but also makes it difficult to integrate with soft materials [23]. Another disadvantage of PZT nanofibers is the low electric conversion efficiency when electrospun, this is mainly due to the added solvents to the mix used for electrospinning. The most conventional PZT energy harvesters are film-based configurations.

PVDF is the most predominant polymer in the field of piezoelectric materials [60] [16]. PVDF has a long-chain, semi crystalline structure with (CH2-CF2) repeat units. PVDF is approximately 55% crystalline [21] and has good piezoelectric and mechanical properties, exhibits chemical stability, biocompatibility [61] and weathering characteristics. It is lightweight and flexible making it a great candidate for wearable energy harvesting. Untreated PVDF can have α, β, γ crystalline phases and must be mechanically stretched and electrically poled to obtain the β phase necessary for enhancing its piezoelectric properties [16]. The fabrication process and characterization of PVDF nanogenerators have been explored in many research papers [62] [61] [63]. In this thesis, nanofiber based generators produced by electrospinning PVDF will be discussed.

1.4.2.1 Piezoelectric Properties

The ability to convert mechanical energy to electrical energy and vice versa is what sets piezoelectric materials apart from other materials. Piezoelectricity is a cross coupling relation between elastic variables (strain and stress) and the dielectric variables (electric displacement and electric field). From the parameters that describe the piezoelectric materials, the two with the highest significance are the piezoelectric constants; d and g. d is the polarization generated per unit of mechanical stress applied to the piezoelectric material, or, the mechanical strain induced by an applied electric field. g relates the open circuit electric field produced by an
applied mechanical stress, or, the mechanical strain developed due to an applied charge density. In experimental evaluations $d$ and $g$ can be evaluated using the following equations:

\[
d = \frac{\text{Strain development}}{\text{Applied electric field}} \left( \frac{m}{V} \right) = \frac{\text{Short circuit charge density}}{\text{Applied mechanical stress}} \left( \frac{C}{N} \right) \tag{1.1}
\]

\[
g = \frac{\text{Open circuit electric field}}{\text{Applied mechanical stress}} \left( \frac{V \cdot m}{N} \right) = \frac{\text{Strained developed}}{\text{Applied charge density}} \left( \frac{m^2}{C} \right) \tag{1.2}
\]

The linear piezoelectric constitutive relations, derived from thermodynamic principles, relate linear elastic relations with linear dielectric relations through the piezoelectric tensor [64]:

\[
S_i = s_{ij}E_j + d_{ki}E_k \tag{1.3}
\]

\[
D_i = d_{ij}E_j + \varepsilon_{ik}E_k \tag{1.4}
\]

Where $i, j$ and $k$ are the 3 spatial dimensions. $S$ and $T$ are strain and stress tensors respectively induced by the mechanical and electrical energy. $D$ and $E$ are the electric displacement and electric field vectors. $S^E$ is the elastic compliance matrix, usually calculated at a constant electric field; $\varepsilon^T$ is the permittivity tensor, evaluated at constant stress [23]. Equations 1.3 and 1.4 can be simplified for situations in which the material is operating in the 33 mode (applied stress is the same direction as the polarization axis) into a relationship between stress and electric displacement:

\[
D = d_{33} \times T \tag{1.5}
\]

Another very important constant is the electromechanical coupling coefficient, $k$, which describes the energy conversion efficiency as the relation between the converted electrical and mechanical energy. The Elastic energy, strain stored energy, represents the mechanical energy of the material and can be calculated using [65] (derived in Appendix D):
where $A$ is the area, $Y$ is the elastic modulus, $L_o$ is the length of the material. In experimental setups the electrical energy stored on the material can be calculated by integrating the power over the time period the measurements are taken [16].

$$W^e = \int_0^t IVdt$$

The energy conversion efficiency is thus found using:

$$k^2 = \frac{W^e}{W^m}$$

PZT fiber composites have been reported to have piezoelectric constants as high as 460 pC N$^{-1}$ compared with 100 for BaTiO3 and 25 for PVDF. Table 1 summarizes the structure and d33 piezoelectric constant for a few different materials and composites.

<table>
<thead>
<tr>
<th>Material</th>
<th>Structure</th>
<th>Piezoelectric Constant d$_{33}$ pCN$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>PZT fiber composite [66]</td>
<td>Composite</td>
<td>~ 260</td>
</tr>
<tr>
<td>PZT-PVDF [67]</td>
<td>Composite</td>
<td>~13-25</td>
</tr>
<tr>
<td>PVDF [66]</td>
<td>Polymer film</td>
<td>-33</td>
</tr>
<tr>
<td>PVDF [61]</td>
<td>Electrospun nanofiber structure</td>
<td>-25</td>
</tr>
<tr>
<td>ZnO [68]</td>
<td>Electrospun nanofiber structure</td>
<td>121</td>
</tr>
</tbody>
</table>

Table 1. Summary of piezoelectric materials and their properties
1.4.2.2 PZT Nanogenerators

Single crystal perovskites, such as PZT have demonstrated very high piezoelectric constants and are remarkably efficient; bulk-ceramic PZT transformers operated at their resonance have shown conversion efficiencies of 80% and more [69]. However, bulk PZT is brittle with limited flexibility. Chen et al. [39] used electrospinning to develop a nanogenerator with fiber diameters of approximately 60nm and 500nm. The nanofibers produced by electrospinning demonstrate high piezoelectric constant ($g_{33}$ of 0.079 Vm/N), high bending flexibility and high mechanical strength when compared to bulk or thin film PZT. Chen et al. [39] aligned the fibers on top of interdigitated thin wire platinum electrodes, which are on a silicon substrate; the whole device is then covered with Polydimethylsiloxan (PDMS). Figure 5 shows the assembly of the fine wires on the silicon substrate. Figure 5 (d) and (e) illustrate the power generation mechanism of the system in which the nanofibers are working in the longitudinal mode with alternating pressure applied on the top surface. The structure was able to provide a voltage output of 1.63V at its highest point. The measured power output of this soft polymer was 0.03 μW using a 6 MΩ load resistance.

In some more recent work Chen et al. [70] have combined electrospinning and lithography to develop a nanogenerator such that the PZT nanofibers work in the $d_{33}$ mode. First the PZT fibers are electrospun on a Silicon substrate, and then gold interdigitated electrodes are evaporated onto the surface. Finally, a polymer coat is placed on top of the device to enhance its mechanical integrity. These nanogenerators were used for acoustic emission sensors and the structure was able to reach 35 mV by picking up acoustic energy from the surroundings.

PZT nanofibers can also be fabricated through a series of lithography and lift-off steps on PZT film. High performing PZT nanomaterial with $d_{33}$ values as high as 140 pmV$^{-1}$ have enabled new electromechanical interfaces [23] for probing small voltages within cellular deflections. Nguyen et al. [71] demonstrated how PZT nanoribbons can be great biosensors for detecting mechanical deformations of neuronal cells in response to electrical excitations. They found that when 120 mV is applied to the cell membrane 1 nm deflection is detected. This experiment agrees with the theories [72] on how the mammalian membranes react to change in tension, in which the cells change their radius so that the pressure across the membrane remains constant.
The experiment continues by transferring the nanoribbons onto a silicon elastomer and the final device is placed on a cow lung that mimics respiration to measure the deformation. Figure 6 includes a schematic and two SEM images of the proposed PZT nanoribbons design. The figure includes a cultured neural cell deposited directly on the PZT ribbons.

Figure 5. PZT nanogenerator (a) Schematic view (b) SEM of PZT mat across interdigitated electrodes (c) cross sectional SEM (d) cross sectional view of polled PZT (e) schematic of power output mechanism [69]
When higher power output is required, the PZT fibers are combined into composite structures in the micro scale. Swallow et al. [66] proposed a microcomposite device consisting of layers of PVDF films and PZT microfibers in the 90-250 μm diameter ranges. As shown in Figure 7, the fibers are laid within a laminate structure with interdigitated copper electrodes. Epoxy is used to insulate the fibers and prevent them from touching each other. Finally a Kapton film coats the two sides of the composite setup. The maximum voltage output from the experimental testing using a cantilever undergoing excitation at 60 Hz was reported to be 6 V.

1.4.2.3 ZnO Nanogenerators

Chen et al. [68] used electrospinning for the fabrication of a nanogenerator using vanadium doped ZnO nanofibers made from a solution that included ZnO, vanadium and polyvinylpyrrolidone (PVP). The produced fibers were calcined at 700° C for the decomposition of the PVP in the electrospun fibers, the final diameters ranged between 150-300 nm. The change in the diameters is demonstrated using SEM imaging in Figure 8. They have shown that the change in the vanadium concentration in the electrospun solution is a driving factor in determining the piezoelectric charge constant, while the $d_{33}$ constant increase from 42 C/N to 121 C/N with
vanadium concentrations in the range of 0.015-0.025, it begins to descend for concentrations higher than 0.025 due to structural deterioration by over doping.

Figure 7. Dimensions and labeling of PVDF layers and PZT fibers [66]

Figure 8. Vanadium doped ZnO (a) XRD (b) SEM before calcination (c) SEM after calcination at 700 [68]
Park et al. [73] used electrospinning to produce a random structure of fibers of ZnO with diameters as low as 35-150 nm, after annealing. They used ZnO in combination with poly (4-vinyl phenol) and ethanol to create an acceptable viscosity in order to conduct electrospinning. The fibers are then annealed at temperatures ranging from 200-800° C to achieve optimal diameter and crystal structure; they conclude that the optimized temperature for the annealing process is between 200-300° C. Sohn et al. [74] developed a sound-driven piezoelectric energy nanogenerator (SPENG) with sufficiently high piezoelectric performance. This ZnO nanofiber design has superior performance in comparison to other vertically grown ZnO nanofibers due to the controlling of the carrier density and the interfacial energy of the semiconductor with a combination of doping and surface modifications. The fabricated Li-doped ZnO nanogenerators with power densities of 0.9 mWcm⁻³, were able to achieve 50 times the current and voltage output of a traditional ZnO nanogenerators. Figure 9 below demonstrates the power capabilities of the SPENG by driving an electrophoretic ink display, based on a voltage drive system without the need of a constant current supply.

![Figure 9](image_url)

Figure 9. Self-powered electrophoretic displays. (a) photograph of the text displayed after sequentially discharging the capacitors (b) Photograph of the display powered by SPENG (c) schematic diagram of the voltage doubling and charge storage circuit [74]

In a recent work by Hu et al. [75], the intrinsic properties of ZnO have been improved by pretreatments of the nanofibers with oxygen plasma, annealing in air and surface passivation with some polymers to enhance performance. They achieved an output voltage of 8 V from a single layer of ZnO fibers, when the fibers were annealed at 350 °C for 30 minutes in air, and the
current output surpassed 900 nA. The measured voltage output when the ZnO fibers were coated with positive charged poly (diallyldimethylammonium chloride) (PDADMAC) and negative charged poly (sodium 4-styrenesulfonate) (PSS), through a layer-by-layer self-assembly method, reached a high of 20 V in correspondence to a power density of 0.2. This is almost 20 times the previously reached power output by ZnO [76].

1.4.2.4 PVDF Nanogenerators

1.4.2.4.1 Aligned PVDF Nanofibers

PVDF nanofibers have proven to be great nanogenerators with sufficiently high piezoelectricity. The PVDF piezoelectricity is only seen in the phase of the polymer. Transformation from the non-polar phase into the polar phase is enhanced by mechanically stretching and electrically poling the nanofibers which in turn aligns the dipoles in the crystal structure of the fiber [77] [78] [79] [80]. The studies of aligning metallic nanofibers conducted by Smith et al. [81] and Duan et al. [82] were one of the first steps towards the study of alignment techniques for nanofibers. Duan et al. utilized electrostatic fields to align Indium Phosphide nanofibers between two electrodes. Tanese et al. [83] used of magnetic fields to align florescent nanofibers in viscous solutions. The magnetic field forces the fibers to form “Chains” in a head-to-tail alignment which is due to the drag forces in the viscous solvent and the magnetic dipole-dipole forces. Nanofibers can also be patterned using micro-molds with micrometer sized channel network. Messer et al. [84] utilized capillary forces to fill nano-molds to shape the nanofibers. By combining fluidic alignment and surface patterning techniques, Huang et al. [85] aligned parallel arrays of nanofibers and displayed controllability of separation in developing one dimensional nanostructures. The channel flow near the surface acts like a shear flow that aligns the nanofibers in the direction of the flow. Theron et al. [14] introduced nanofiber alignment via a tapered drum as seen in Figure 10. The tangential force stretched the fibers and consequently reduced their diameters. Recent developments in far field electrospinning (FFES) and near field electrospinning (NFES) further simplified the process of nanofiber alignments [16] [86].

Byun et al. [87] utilized the electrospinning concepts to fabricate aligned and patterned PVDF sheets. A grounded drum collector covered with Polyethylene terephthalate (PET) shown in Figure 11 demonstrates an in-situ mechanical stretching as well as electrical poling of the nanofibers. In the experimental setup, a textile-like piezoelectric surface resulted from
electrospinning of a PVDF solution in DMAC and acetone at a voltage of 6-15 kV and a needle to ground distance of 7-15 cm. The flow rate of the solution was controlled and maintained at 0.4-1 mL/h from the needle outlet.

![Diagram of electrospinning setup]

Figure 10. Schematic and actual photograph of collecting nanofibers on a thin drum [14]

Using PET rather than a metallic collector, on the grounded drum, resulted in a surface that had both aligned and non-aligned fibers. As seen in Figure 11, the aligned fibers are clear and the randomly positioned are opaque. Investigations showed that since PET is non-conductive, some parts of the collector were grounded and some parts were left ungrounded; the aligned fibers were formed on the parts that were not grounded. Thus it seems that there was a dual collector formed on the PET sheet. This forced the polymer jet to “jump” from one grounded area to the next and in doing so stretch across the ungrounded gaps.

The direct write technique proposed by Chang et al. utilizes near filed electrospinning [17] [18] to produce and deposit PVDF nanofibers with in-situ mechanical stretching and electrical poling to ensure the PVDF is in the polar phase (i.e. aligned dipoles and enhanced piezoelectricity) [16]. Figure 12 demonstrates the experiment setup, which includes the use of two metallic electrodes as the ground for electrospinning; the distance between the electrodes is 100-600 μm, which determines the length of the fibers. The diameters of the nanofibers range from 500 nm to 6.5 μm.
When the nanofibers, deposited on a flexible plastic substrate, are exposed to a stress in the direction of the aligned dipoles along the axial path the piezoelectric potential constant, $d_{33}$, and piezoelectric charge constants, $g_{33}$, are responsible for the piezoelectric responses. Periodic stretch and release of the fiber resulted in voltage and current outputs of 5-30 mV and 0.5-3 nA respectively. The study showed that the output current of the PVDF nanogenerator increases with increase in the strain rate whereas the total charge generated are the same under different strain rates while maintaining the same applied total strain.

Figure 11. PVDF nanofiber mats (a) photograph of electrospun mat. SEM of aligned (b) and non-aligned (c) PVDF. (d) Aligned clear portion and (e) opaque portion of the mat [87]

It is found that the output voltage and current of PVDF nanogenerators, subjected to continuous stretch and release, can be enhanced if the nanogenerators are connected in series and parallel respectively. The effect of joining two nanogenerators in serial and parallel connections will
result in approximately the sum of the individual nanogenerators, which agrees with the “linear superposition” law proposed by Yang et al. [88] to validate true piezoelectricity.

A hybrid energy harvester designed to harvest both mechanical and biochemical energy has been developed by Hansen et al. [89]. The Electrospun fibers were collected on the grounded copper electrodes. The length of the fibers, which is determined by the gap between the copper electrodes, was around 2 cm. The fibers were then transferred, manually, to a Kapton thin film to be poled. A 0.5 mm layer of PDMS was deposited over the device, for dielectric protection and biocompatibility, and the device was dipped in paraffin oil. Finally, 20 kV was applied for 15 minutes to increase the piezoelectric response of the device by a secondary poling of the piezoelectric fibers. Figure 13 shows the electrospinning setup as well as the poling technique. The experimental results are consistent with the piezoelectric theory [90] on dependence of the open loop voltage and short circuit current on strain rate. The increase in strain rate, while total strain is constant at 0.05%, resulted in an increase in voltage, as high as 20mV, and increase in

Figure 12. PVDF Nanogenerator (a)Near Field Electrospinning causing both electrical poling and mechanical stretching (b) SEM of a single fiber (c) Output voltage and (d) current measured at 2Hz [16]
short circuit current, as high as 0.3 nA. The final conclusion of the experiment was that further improvement of power output would result by integrating the devices in parallel and/or series.

Figure 13. (a) schematic of the electrospinning process (b) SEM of a single fiber and the optical image of the fibers on Kapton film (c) FTIR transmission spectrum of the PVDF nanofibers (d) in-plane poling of the fibers [89]

1.4.2.4.2 Non-Aligned PVDF Nanofibers

Non-aligned PDVF based nanogenerators are typically fabricated by conventional electrospinning, which transforms the PVDF into the β phase crystal structure. Baji et al. [91] studied these fibers in depth and used characterization tools such as XRD (X-ray diffraction), FTIR (Fourier Transform Infrared) spectra and hysteresis loops under PFM (Piezoresponse Force Microscopy) to demonstrate that after electrospinning and without secondary poling, the polar β phase was the dominant crystal phase. The reason would be the high electrostatic forces as well as the extensional forces induced on the polymer during the electrospinning process. Another important finding by Baji et al. [91] was the importance of the fiber diameter in the presence of the β phase. A reduction in the fiber diameter increased the β crystal formation. In an experiment done by Fang et al. [40] a 140 µm thick active layer of PVDF nanogenerator was produced by far field electrospinning without any extra poling treatment and the piezoelectric response was studied. At high compression impact frequencies the output voltage of a 2 cm² active area is as high as 6.3 V as seen in Figure 14 and the energy conversion efficiency of about 14%. 
Figure 14. Power generation setup
(a) schematic of the setup (b) Typical voltage output due to initial impact speed of 34mm/s (c) Voltage and (d) current outputs under 5 Hz repeated compressive impact [40]

Mandal et al. [92] used a copolymer of PVDF, polyvinylidene fluoride-trifluorothylene [P(VDFTrFE)], because unlike PVDF that has different crystalline phases, PVDF-TrFE only has one ferroelectric crystalline structure (β phase) below the Curie transition temperature (Tc).

Using conventional electrospinning, as seen in in Figure 15, with a drum collector covered with Ni-Cu plated polyester fabric, a web of nanofibers was produced. With a thickness of 43mm PVDF the maximum output voltage under a constant strain rate was around 0.4V. The voltage output, under the same strain rate, of as-electrospun fibers and annealed fibers are shown in in Figure 16. The graphs clearly demonstrate the effect of annealing on the voltage output; the heat randomizes the dipole directions and reduces piezoelectricity. In order to determine the orientation of the structure two setups were tested. The first graph, in Figure 16 (B-a), is a series structure with top-bottom-top-bottom setup. The sample in the second graph, in Figure 16 (B-b), has a bottom-top-top-bottom stacked structure. In comparison to the output seen in Figure 16 (A) the output signal was doubled in structure (a) where the output signal of structure (b) has been almost diminished.
Figure 15. Schematic of electrospinning the PVDF mat [92]

Figure 16. (A) Piezoelectric Voltage output of the P(VDF-TrEF) mat with a periodic pressure frequency of 5.3Hz heat treated and as-electrospun. (B) Piezoelectric output signals from structures (a) and (b) [92]
1.4.2.5 Characterization Methods

In this section three methods of characterizing piezoelectric materials will be introduced. The surface properties of the nanofibers are investigated using the Scanning Electron Microscope (SEM) to ensure consistency in surface conditions and diameter. Detecting of webs, droplets and breakage of the fibers can be done with an SEM. Atomic Force Microscopy (AFM) has a vast range of capabilities, but in the case of piezoelectric nanofibers and nanomaterial AFM provides information about the material and mechanical properties of the fibers, including the Young’s modulus, permittivity and adhesion of the fibers. Piezoelectric Force Microscopy (PFM) is a great way to investigate the local piezoelectric properties of the nanomaterial. PFM provides the local deformation of the nanofibers due to an applied bias voltage, making it easier to calculate the piezoelectric properties of unknown piezoelectric materials. The combination of these three methods provides the necessary tools to characterize a material that has not been studied before. Piezoelectric constants and material properties of many nanofibers, polymer nanofibers in particular, have not been identified and so these tools provide great capabilities to researchers and scientists.

1.4.2.5.1 Scanning Electron Microscope

The scanning electron microscope (SEM) provides detailed images of the specimens by means of shooting high-energy electrons to the surface of the specimen. The sum of the reflections of the electrons describes the morphology and crystal structure of the samples. The resulting signals from the SEM provide information about the sample’s external texture, chemical compositions and crystalline structure. Figure 17 demonstrates what an SEM setup would look like. Almost all researchers in the field of nanofabrication use SEM for analysis and tracking of their progress. Kameoka et al. [93] have one of the most interesting demonstrations of the use of SEM in process optimization of the nanofibers. In the process of analyzing the influence of deposition distance, when electrospinning polyethylene oxide (PEO), on the nanofiber diameter they used SEM to track the changes while the distance was changed from 0.5 to 1.5 cm as seen in Figure 19. Theron et al. [14] have used SEM to validate their concept with braided nanofibers made on thin drums as seen in Figure 18 below.
Figure 17. Photograph of an SEM setup including a blown-up schematic of the inside of the microscope on the right [94]

Figure 18. Braid of PVDF nanofibers [14]
1.4.2.5.2 Atomic Force Microscopy

Atomic Force Microscopy is the analysis of the sample surface by bringing the sample and the probe in the proximity of each other. The probe and sample move relative to each other at a very slow speed in a raster pattern and the measure quantity is in a serial display at discrete locations (pixel like). Figure 21 shows a schematic of the cantilever setup in an AFM. Any displacement of the free end of the cantilever is recorded to display the interactions between the probe and the surface of the sample. Baji et al. [91] have used AFM to test the morphology of the fabricated PVDF nanofibers as seen in Figure 20.
1.4.2.5.3 Piezoresponse Force Microscopy

Piezoresponse force microscopy relies on the detection of local deformation of the ferroelectric sample. An externally applied bias voltage encourages the deformation. This dynamic piezoresponse imaging method is based on the application of an AC modulation voltage on to the sample and the sample topography variations are detected using a standard lock-in technique by detecting the vertical vibration of the cantilever as seen in Figure 22 [96].
In the case of nanofibers, PFM provides the most insight when the poling direction is parallel to the voltage bias applied. It will provide “in phase” response and if the voltage is the opposite of the poling direction it will result in 180 degrees “out of phase” results. PFM setup is comparable to AFM and most often an AFM setup with a probe bias tip in very close proximity of the sample surface is used. It has prominently better performance when a single nanofiber is being characterized with respect to the material in its close vicinity. Isakov et al. [97] demonstrate this prominent capability by analyzing the piezoelectricity and ferroelectricity of triglycine sulfate (TGS) nanocrystals embedded in electrospun PEO nanofibers. Figure 23 shows the topography and piezoelectric response of the TGS-PEO electrospun mat. Figure 23 (b) demonstrates the vertical PFM that can result in the evaluation of the $d_{33}$ value whereas Figure 23 (c) is the result of the lateral PFM used for the calculation of the effective $d_{15}$ value.
1.5 Contributions

To explore the possibilities of fabricating a flexible nanogenerator this thesis presents a technique for the fabrication of a flexible nanogenerator using a piezoelectric polymer. The contributions of this research project are listed below.

- Conducted a study and analyzed existing method of fabricating nanogenerators.
- Provided a comprehensive summary of the preexisting knowledge about PVDF nanogenerators and their fabrication using electrospinning.
- Developed a repeatable technique for the making of the PVDF solution to be electrospun.
- Conducted various experiments on collectors for electrospinning to conclude on the optimal electrospinning parameters.
- Fabricated a nanofabric with the PVDF solution using the electrospinning method.
- Prepared a flexible nanofabric capable of generating $2200 \frac{pw}{cm^2}$ of power. The nanofabric production method is scalable and feasible to be manufactured in large scales.
Chapter 2

2 MATERIAL SELECTION AND FABRICATION OF THE NANOFABRIC

2.1 Introduction

This chapter will discuss the experimental steps used for the fabrication of the PVDF nanofabric. The chapter begins by introducing the material used for the fabrication, the main factors in the material selection and the manufacturing process. The section continues with an introduction to the fabrication process of the nanofibers and the nanofabric. This will include the electrospinning conditions and parameters. Characterization is the final section in this chapter. The characterization methods discussed in the previous chapter will be used to analyze the fabricated nanofiber to insure piezoelectricity.

2.2 Material Selection

PVDF has proven to be a great piezoelectric material; it is chemically stable and bio compatible [61] with great mechanical properties. As mentioned in the previous chapter, PVDF acts as a piezoelectric material when the polymer is in the β phase. The transformation from the α phase occurs by mechanically stretching and electrically poling the material, which aligns the dipoles in the crystal structure of the material, demonstrated in Figure 24. Electrospinning causes in-situ polarization and stretching of PVDF nanofibers [77] [78] [79] [80]. Ren et al. [98] verified the effect of electrospinning on PVDF by extensive characterization analysis on the fabricated nanofibers through use of X-ray diffraction (XRD) and Fourier transform infrared spectroscopy (FTIR). The study concluded that electrospinning converts α phase of plain PVDF into the β phase. Table 2 summarizes the solvents and electrospinning parameters used by previous researchers for the electrospinning of PVDF nanofibers.

2.2.1 The Effect of Solution Properties in Electrospinning

The electrospinning process is driven by the following parameters: solution properties including viscosity, conductivity and surface tension; electrospinning setup variables including the hydrostatic pressure in the nozzle, applied electric field and tip to collector distance; environmental parameters including the temperature and humidity in the vicinity of the
electrospinning setup [99]. All of the electrospinning done for this project have been performed within a confined chamber at room temperature and the tip to collector distance was kept small enough to avoid the environmental effects. The electrospinning parameters will be discussed in detail in section 2.3.1 of this report. This section will discuss the importance of the solution parameters.

![PVDF crystal structure in alpha and beta phase](image)

**Figure 24. PVDF crystal structure in alpha and beta phase**

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Range</th>
</tr>
</thead>
<tbody>
<tr>
<td>Solvents</td>
<td>DMAC, DMF, Acetone</td>
</tr>
<tr>
<td>PVDF Concentration</td>
<td>5-25 wt%</td>
</tr>
<tr>
<td>Applied voltage during electrospinning</td>
<td>10-25 kV</td>
</tr>
<tr>
<td>Tip to collector distance during electrospinning</td>
<td>5-30 cm</td>
</tr>
<tr>
<td>Solution flow rate during electrospinning</td>
<td>0.4-15 ml/hr</td>
</tr>
</tbody>
</table>

*Table 2. Summary of PVDF solution and electrospinning parameters*

For the case of this project in which PVDF is in a DMF/acetone mixture, the viscosity and surface tension of the polymer solution are affected by the amount of acetone, the polymer
concentration and the addition of surfactant. As seen in Figure 25, polymer concentration introduces intermolecular interactions; hence increase in the polymer concentration increases the intermolecular interactions, which result in an increase in both viscosity and surface tension. The solution mix of DMF and acetone play a very important role in the viscosity of the final mixture. The low viscosity and density of acetone leads to an overall decrease in the viscosity of the mixture while introducing high volatility to the polymer solution. Excessive acetone in the mix can result in the sudden change of surface properties and fast drying of the polymer during the electrospinning process. The addition of surfactant to the solution will reduce both the surface tension and viscosity of the material.

![Diagram showing the relationship between surface tension and viscosity with polymer concentration and surfactant addition.]

**Figure 25. The affect of solution parameters in the material behavior of the PVDF solution**

Considering the concepts mentioned above the following steps were taken for the preparation of the material used for electrospinning PVDF nanofibers:

- Deciding on the PVDF concentration
- Deciding on the DMF/acetone ratio
- Preparation setup design (mixing temperature and speed)
The first two steps happen in parallel, and so the third step is based on the outcome of steps 1 and 2. In the following section these steps will be discussed in more detail.

2.2.2 Polymer Solution Preparation

Various solution combinations were considered for the study and optimization of the PVDF solution but the steps taken for the preparation of the electrospinning solution can be generalized into the following:

- The N,N-Dimethylformamide (DMF) (99.5% Bioshop) and acetone (99.5% Caledon) are weighted and mixed together, depending on the testing ratio.

- The PVDF powder (Alfa Aesar) is weighted and added to the mixture.

- This combination is then placed on a magnetic stirrer with a heated plate (Scilogex MS-H-pro). The temperature of the plate and stirring play an important role in the formation of the nanofibers during electrospinning.

- The solution will have bubbles and so the mixture is left to cool down for about 20 minutes before beginning the electrospinning.

In the case of traditional electrospinning, the applied voltage is much higher than that of NFES [16] and so the addition of surfactants is not necessary. This is because the applied voltage is high enough to overcome the surface tension. In the case of NFES the applied electric voltage cannot overcome the surface tension and so surfactant is added to reduce the viscosity and surface tension of the material [100]. The Solution preparation for this project was at room temperature. To minimize the acetone evaporation, the containers were all sealed and the solution was electrospun immediately after preparation. The evaporation causes the solution to thicken and solidify; all of the samples examined in this project were electrospun within an hour of solution preparation. Table 3 summarizes some of the experimental parameters used for the solution preparation. DMF and DMAC are the two solvents mixed with acetone. The last row in the table is from a set of tests done with Tetramethylammonium chloride (TMAC) as an additive. In theory additives enhance alignment and conductivity of the solution [101] however in the experimental analysis done for this project did not show any significant changes with the presence of TMAC. Using a microscope the nanofibers were analyzed. It was observed that the
nanofiber alignment of the nanofabric made using the solution with TMAC was not any different from the nanofibers made without the TMAC, fabricated under the same electrospinning condition. Hence, the effect of adding TMAC was low enough to be neglected.

Table 3. Summary of experimental parameters for the preparation of PVDF solution

<table>
<thead>
<tr>
<th>Solution No.</th>
<th>PVDF ratio (PVDF/solution)</th>
<th>PVDF weight (g)</th>
<th>Solvents</th>
<th>Solvent Ratio</th>
<th>Stirring Temperature (°C)</th>
<th>Stirring speed (RPM)</th>
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<tbody>
<tr>
<td>1</td>
<td>15%</td>
<td>15</td>
<td>DMF: Acetone</td>
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<td>600</td>
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<tr>
<td>2</td>
<td>12%</td>
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<td>DMF: Acetone</td>
<td>2:3</td>
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<td>210</td>
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<tr>
<td>3</td>
<td>20%</td>
<td>20</td>
<td>DMAC: Acetone</td>
<td>1:1</td>
<td>25</td>
<td>300</td>
</tr>
<tr>
<td>4</td>
<td>16%</td>
<td>16</td>
<td>DMAC: Acetone</td>
<td>2:1</td>
<td>25</td>
<td>300</td>
</tr>
<tr>
<td>5</td>
<td>13%</td>
<td>3.25</td>
<td>DMF: Acetone</td>
<td>2:3</td>
<td>60</td>
<td>300</td>
</tr>
<tr>
<td>6</td>
<td>12%</td>
<td>3</td>
<td>DMF: Acetone</td>
<td>2:3</td>
<td>25</td>
<td>120</td>
</tr>
<tr>
<td>7</td>
<td>12%</td>
<td>3</td>
<td>DMF: Acetone</td>
<td>2:3</td>
<td>60</td>
<td>120</td>
</tr>
<tr>
<td>8</td>
<td>11%</td>
<td>2.75</td>
<td>DMF: Acetone</td>
<td>2:3</td>
<td>35</td>
<td>200</td>
</tr>
<tr>
<td>9</td>
<td>12%</td>
<td>3</td>
<td>DMF: Acetone</td>
<td>1:2</td>
<td>60</td>
<td>300</td>
</tr>
<tr>
<td>10</td>
<td>15%</td>
<td>3</td>
<td>DMF: Acetone</td>
<td>2:3</td>
<td>60</td>
<td>300</td>
</tr>
<tr>
<td>11</td>
<td>14%</td>
<td>2.8</td>
<td>DMF: Acetone</td>
<td>2:3</td>
<td>65</td>
<td>400</td>
</tr>
<tr>
<td>12</td>
<td>16%</td>
<td>3.2</td>
<td>DMF: Acetone</td>
<td>2:3</td>
<td>65</td>
<td>400</td>
</tr>
<tr>
<td>13</td>
<td>15%</td>
<td>3 gr PVDF +0.5gr TMAC</td>
<td>DMF: Acetone</td>
<td>2:3</td>
<td>65</td>
<td>400</td>
</tr>
</tbody>
</table>

Figure 26 provides a visual summary of the table above except for the last row. As it can be seen that very small changes in the polymer concentration or solvent ratios dramatically affects the fibers development process. SEM and microscopic images were the first tools used for the optimization of the fiber diameter and consistency. Material preparation parameters, the polymer concentration in particular, provide control over the fiber formation and consistency of the diameter. The effects of electrospinning parameters on the diameter and fabric density will be discussed in the following sections.
2.2.3 Polymer Solution Optimization

The weight ratio of PVDF in the solution has a direct effect on the polymer viscosity and its ability to be electrospun. To demonstrate the importance of optimizing the polymer concentration, three samples with exact DMF to acetone ratio and different polymer concentrations are considered. The first sample includes 13 wt% PVDF in a 2:3 DMF: acetone ratio solvent. As it can be seen in Figure 27 (A), both fibers and webs are present in this sample. Figure 27 (B) and (C) have very similar PVDF ratios, (B) has 16% and (C) has 15%, and there are only fibers in the samples. The major difference detected was the increase in controllability of the diameter when the PVDF concentration was between 14-15 wt%.

Figure 26. Graphical summary of the experiments using SEM and microscopic images
A simple test was conducted to compare DMAC with DMF as the primary solvents to be mixed with acetone. Different DMAC and acetone ratios were considered and SEM was used to verify the status of the electrospun samples. Two observations were made when considering DMAC; the first was in regards to the DMAC to acetone ratio. When the amount of DMAC content in the mixture is more than the acetone concentration, the electrospinning process is inconsistent. The surface tension of the material increases and the electrospinning process turns into electrospraying, in which the polymer sprays and creates webs of PVDF. Figure 28 (C) is a great...
demonstration of this phenomenon. This particular experiment had 16wt% PVDF and the ratio of DMAC to acetone was 4:2, resulting in webs and spattered PVDF. The second observation was in regards to the diameter of the fibers fabricated with the DMAC solution. Even when the ratio of DMAC to acetone is optimized the diameter of electrospun fibers are much larger, almost 7 times larger, than the diameter of the fibers fabricated with DMF solution. Figure 28 (A) and (B) are SEM results from one of the samples with the least percentage of inconsistency of fiber diameter. It can be seen that the smallest diameter reached is around 3 μm.

Due to the difficulties of controlling the fiber diameters, DMF was chosen as the solvent of choice. The ratio of DMF to acetone controls the viscosity and dry time of the fibers. The solution will have less viscosity with the increase of acetone and if the amount of acetone in the mixture is too high the electrospun fibers will dry too fast. The lack of acetone causes more problems since the nanofibers don’t dry fast enough and merge on the collector resulting in a single sheet of PVDF plastic.

Figure 28. SEM of electrospun PVDF made with DMAC and acetone as solvents (A) 20wt% PVDF 1:1 DMAC :acetone (B) Magnified image of (A) . (C) 16wt%PVDF 4:2 DMAC:acetone
Figure 29. Electrospun PVDF with 15wt% PVDF concentration (A) 1:1 DMF: acetone (B) 1:2 DMF: acetone (C) 2:3 DMF: acetone ratio

Figure 29 includes three different electrospun PVDF solutions with different DMF to acetone ratio. Figure 29 (A) is a typical case of electrospun fibers when the surface tension is too high, the solution in this case has 1:1 DMF to acetone ratio. The lack of acetone in the solution results in an increase in the surface tension, which has a direct effect on the consistency of the fiber diameters across its length. Figure 29 (B) is electrospun PVDF with 1:2 DMF to acetone ratio solvent mixture. In this case the fibers dried too quickly. The fibers did not form complete string-like fibers; rather they would stroke the collector like a thin line of paint. The low viscosity of the solution causes the fibers to lose their form before drying. After many tests and reconsiderations an optimum DMF to acetone ratio was chosen. Figure 29 (C) is a microscopic image of an electrospun PVDF solution with 2:3 DMF to acetone ratio. It is worth mentioning
that the control of the diameter of the fibers, lack of bubbles in the sample and fiber consistency requires optimization of both the solution properties and electrospinning parameters.

The final material preparation parameter to consider is the stirring speed and temperature at which the solution is made. The relatively high temperature allows the crystalline polymer to completely dissolve and form a homogenous solution. The temperature at which the solution is prepared is a key factor for the formation of the fibers and electrospinning behavior of the solution. If the preparation temperature is not high enough the solution will not be homogeneous and the electrospinning will begin to look more like electrospraying of the PVDF crystalline particles. As seen in Table 3, 65°C was chosen as the optimized temperature for sample preparation.

2.3 Fabrication of the PVDF Nanofabric

After the polymer solution has been prepared the electrospinning process begins. In the following sections the electrospinning parameters and optimization techniques have been discussed in detail.

2.3.1 Electrospinning Optimization

Two different electrospinning methods were considered for the fabrication of the PVDF nanofibers. The first method uses a cylindrical drum as the grounded collector for the nanofibers. Figure 30 demonstrates the setup used for the first set of PVDF nanofibers fabricated with electrospinning. The fibers produced using this method result in randomly oriented nanofibers with uncontrollable direction and alignment. The average distance between the nozzle tip and the collector is 10cm while the average applied voltage is 19 kV. As discussed in the next section the nozzle diameter was kept at 0.8 mm. This conventional method allows for high speed fabrication of thick nanofabrics. The produced fabrics are durable with thicknesses ranging from 80 μm to 120 μm. The desired the electrospun nanofabric is opaque and white in color. Figure 31 is an example of a non-piezoelectric sample fabricated with this method; a microscopic image shows the lack of consistent fibers in a section of the fabricated nanofabric.
Based on the observations made during the experimental developments, there can be two reasons for which the PVDF nanofabric is clear: the first is lack of electrical poling during the electrospinning process; and the second is the electrospinning of a non-homogenous PVDF solution. In the case of Figure 31 the solution used was homogeneous and so the clarity of the nanofabric is mainly due to lack of electrical poling of the PVDF fibers. The problem with small applied electric field can be solved by either increasing the applied voltage and/or reducing the distance between the nozzle and the collector. The testing of the piezoelectricity of this sample will be discussed in the next chapter of this thesis. Figure 32 is an example of a piezoelectric nanofabric that is both white and opaque fabricated with the same electrospinning method.
The second method considered was inspired by the NFES method introduced by Chang et al. [16]. The two electrode collector method, shown in Figure 12, has very small nozzle tip to collector distance. The fiber is stretched between the two electrodes with a small gap. The drum collector in Figure 30 is replaced by the collector seen in Figure 33A. This collector includes two aluminum blocks mounted on a thick polyvinyl chloride (PVC) board. The electrodes are grounded using the two wires seen in the figure, see Appendix A for engineering drawing of the collector. The gap between the conductive electrodes forces the nanofibers to stretch between the
Electrodes. Figure 33 (B) is an image of electrospun nanofibers using this setup. This arrangement is very fragile and the relocation of the fibers from the electrospinning setup causes the fibers to break. Figure 34 is an SEM of one of the samples made from this setup. The majority of the fibers are aligned and horizontally stretched across the two sides. This method cannot fabricate nanofabrics in a large scale fabrication setup since the fibers are fragile and can’t be separated from the aluminum electrodes without breaking.

Figure 33. Electrospinning using two electrodes (A) image of the two electrodes collector (B) Photo of the nanofibers stretched between the two electrodes

Figure 34. SEM of electrospun PVDF using two electrode collector setup

The next fabrication technique combined the previously mentioned techniques such that nonconductive regions within the drum collector created gaps of non-conductive areas. In this setup Polyethylene terephthalate (PET) arrays create nonconductive regions that force the fibers to stretch across them. This method is basically combining the theory of the second method mentioned above and the practicality of the first method.
Using this method, the first layers of the nanofibers stretched and aligned across the PET arrays. After a few more layers accumulated, the effect of the PET array started to diminish. A microscopic view of the first layers displayed sparse aligned nanofibers on the PET regions. But after 30 minutes of electrospinning using the combined collector, the surface of the nanofabric looked no different than the surface of the nanofabric electrospun using the simple drum, Figure 32. Hence it was decided to continue the experiments with the simple drum collector.

Figure 35. Proposed collector design with nonconductive Polyethylene Terephthalate (PET) array

The simple drum method does not provide aligned nanofibers, rather woven fibers forming a nanofabric. This durable fabric demonstrates great piezoelectricity with promising power output. The fabrication process of this nanofabric can be easily scaled to work in larger manufacturing facilities.

2.3.2 Process Parameters

Considering the material parameter optimization process was completed by the fabrication of the fibers via electrospinning, it is valid to say the optimization of both was done in parallel. Electrospinning parameters considered include the applied voltage, the electrode to collector distance, the nozzle tip and the polymer flow rate. Each of these parameters has an impact on the fiber diameter, formation of bubbles and dry time of the nanofabric. These parameters will be
discussed in detail in the following sections. Other parameters that can affect the performance of the electrospinning process include the drum rotation speed, environmental temperature and the humidity of the surrounding air. For the purpose of this project these variables are kept constant for the fabrication of all samples.

2.3.2.1 Applied Voltage and Electrode to Collector Distance

The applied voltage and electrode to collector distance have been combined since their effect on the polymer fibers and behavior are interrelated. Researchers have studied the direct impacts of applied voltage and fiber diameter with dissimilar results. Nasir et al. [102] concluded that an increase in applied voltage resulted in an increase in the diameter of the PVDF nanofibers whereas Andrew et al. [103] and Gao et al. [104] reported a decrease of diameter with an increase in the applied voltage. The change in the diameter with respect to the applied voltage cannot be easily generalized since the PVDF solution and the collector to nozzle tip distance vary from experiment to experiment.

For the case of this project, where the electrospun solution is 15 wt% PVDF with 2:3 DMF to acetone ratio solution, a decrease in the diameter of the fibers with an increase in the applied electric field was observed. The applied electric voltage and the nozzle distance make up for the applied electric field. The electric field directly influences the d_{33} value of the electrospun nanofabric. Figure 36 displays the relationship between the applied voltage and nozzle tip to collector distance for 18 samples of 15 wt% PVDF and 2:3 DMF to acetone ratio. The blue dots are the required voltage for the formation of the Taylor cone (i.e. initiation of electrospinning) and the red points mark the voltage at which the process becomes steady and the nanofabric formation begins. The figure shows that if the nozzle to collector distance is around 8 cm, the required voltage to initiate the electrospinning process is between 14-17 kV. An additional 5-6 kV are required before reaching a steady electrospinning state, which mean at 8 cm distance 19-23 kV is required to have a stable electrospinning process. This range of voltage needed for the initiation of the electrospinning process for the same nozzle to collector distance can be due to small experimental and measurement errors.
The nozzles size and inner diameter have a direct effect on the fiber diameter and its consistency. The two nozzles used for the fabrication of the nanofabric were both brass nozzles with 0.8mm inner diameter, Figure 37. When a larger nozzle is used for electrospinning, the polymer solution has to travel a longer distance before reaching the nozzle tip. Figure 37 (A) is the initial nozzle used for the electrospinning process and it was found that the nozzle shown in Figure 37 (B) can replace it to increase the nanofiber quality. The smaller nozzle has the same inner diameter of 0.8 mm but since the path is shorter, the risk of bubble formation before the solution reaches the nozzle tip is dramatically reduced. Figure 38 includes microscopic images to compare the electrospun fibers with the two nozzles in Figure 37. Both experiments are conducted with 15 wt% PVDF in a 2:3 DMF to acetone ratio solvent. It can be clearly seen that the nanofabric made with the larger nozzle has a higher number of bubbles and this number is dramatically reduced when the nanofabric is made with the smaller nozzle.
2.3.2.3 PVDF Flow Rate

The flow rate at which the PVDF solution is fed to the nozzle determines the availability of the liquid to be electrospun at any instantaneous time. This means if the flow rate is too low, the electrospinning process stops until there is enough polymer solution at the tip to continue the electrospinning again. This causes breakage of the fibers. When the flow rate is not enough, the electrospinning process becomes more like electrospraying due to the continuous breaking of the fibers. This causes the formation of webs rather than woven fibers. The excess flow of polymer solution can also cause problems, especially when the electric field is still not high enough to begin the electrospinning process. The excess polymer causes the Taylor cone to grow into a large droplet. Once the electric field is high enough to begin electrospinning, more than one
strand of fibers will begin to emit from the droplet since the surface area is so large. This will impact the controllability of collecting the electrospun nanofibers. The flow rates used for the electrospinning of the PVDF nanofabric vary from 6 ml/hr to 9 ml/hr.

2.3.3 Fabrication of PVDF Nanofabric

The PVDF solution was filled into a syringe and placed in the mechanical pump, as seen in Figure 30. The flow rate was set using the mechanical pump, in the range of 6 ml/hr to 9 ml/hr. The distance between the nozzle tip and the grounded drum was controlled using the electrospinning device’s controller in the front panel seen in Figure 30. The distance used ranged from 7-12 cm. The voltage bias was applied to the nozzle, as seen in Figure 40, and the drum collector was grounded. Figure 40 is a schematic of the electrospinning process. The applied voltage before the onset of electrospinning ranged from 10-25 kV but the optimum samples were fabricated with applied voltages of 18-22 kV. The drum rotation speed was kept at 50 rpm for the fabrication of all samples. This process was repeated over 30 times to understand the repeatability of the fabrication parameters as well as produce samples that were good enough to be considered for detailed characterization and testing. The diameter of the nanofibers in the nanofabric was not always consistent and uniform, as seen in Figure 39, and the samples with the most consistent fibers were chosen for further testing and characterization.

Figure 39. Optical images of three different PVDF samples with non-uniform fibers
2.4 Characterization of Nanofabrics

The characterization analysis of the electrospun PVDF nanofabric will be presented in this section. First, the piezoelectric behavior of the nanofabric will be discussed to validate the attempt to fabricate piezoelectric nanofabrics. Then the mechanical properties of the PVDF nanofabric will be discussed, this is particularly important if this method is to be scaled to a larger manufacturing setup.

2.4.1 Piezoresponse Force Microscopy (PFM)

PFM was used to record the displacement and responses of the sample towards an applied bias voltage. The PFM testing setup was designed using a Bruker Atomic Force Microscope.
2.4.1.1 PFM Sample Preparation

The electrospinning solution was prepared by dissolving 15wt% PVDF powder in a 2 to 3 DMF to acetone ratio solvent mixture, at 65°C. The electrospinning parameters include an applied voltage of 19 kV with 8 cm nozzle to grounded collector spacing and a polymer flow rate of 6 ml/hr. The electrospun PVDF nanofabric was then attached to the sampling glass using silver paint. The setup shown in Figure 41 includes the silver paint, which acts as both an adhesive for attaching the fabric as well as an electrode for the PFM process. The fabric thickness is 100 µm. The 3D image in Figure 42 is the topography of the 25 by 12.5 µm² scanned areas showing the non-aligned nanofibers within the nanofabric. The non-alignment can also be seen in the microscopic image of the nanofabric in Figure 41. The fibers constituting the nanofabric have consistent diameters averaging at 1 µm.

2.4.1.2 PFM Parameters

A Bruker AFM device was used to perform the PFM using an MESP-RC probe. The probe deflection sensitivity and spring constant were found during the calibration to be 14.77 nm/V and 4.217 N/m, respectively. The applied voltage to the tip of the AFM probe (Figure 41) was 2444 mV and the silver electrode on the bottom surface of the nanofabric was grounded.

Figure 41. A) Sample attached to the glass and microscopic view of the sample. B) Standard PFM setup [96]
Figure 42. 3D image of a 25 by 12 \( \mu m^2 \) surface area of the PVDF fabric developed using Bruker AFM device under applied voltage bias of 2.4V
2.4.1.3 PFM Results and Analysis

Using PFM, the surface of the fibers was analyzed to find the ferroelectric domains and piezoresponses. The nanofabric proved to be piezoelectric since the voltage bias caused local structural deformation, detected by the probe cantilever and acquired via the lock-in amplifier circuit. PFM works as a tool for comparing different sections of the surface; in this case it compares the piezoelectricity of the single fibers on the top layer versus the underlying mat. Figure 42 includes two dimensional images of the height and the amplitude response (the bottom two images). These two figures display the correspondence between the location of the fibers and the piezoresponse they had when 2.4V of bias voltage was applied.

Figure 43 shows both the amplitude and phase response of the sample in a three dimensional map. Figure 43A is the amplitude response; the piezoresponse of the nanofabric becomes clear when compared to the silver paint on the side (orange rectangle in the figure). The nanofabric material has a noticeably higher amplitude. The sample has a uniform change of amplitude across the nanofibers (mainly green and blue color); except for the noise like changes on the edge of the fibers (pink colored spikes). It is found that the tip of the AFM probe can easily slip around the edges of the fibers causing irregular responses. Both Figure 43(A) and Figure 43 (B) can be compared to the top figure in Figure 42 for analyzing the surface of the nanofabric. The phase response, Figure 43 (B), has similar behavior as the amplitude response in that it has noise like values at the edge of the fibers and uniform values everywhere else.

In order to calculate an effective $d_{33}$, the mean amplitude of the PFM response was measured using a roughness test on the PFM amplitude results. The box was drawn to limit the analysis to the PVDF nanofabric and not include the silver electrode. As seen in Figure 44 the mean amplitude across the area of the sample is 0.132 nm. The data within the selected box has a standard deviation (Rq) of 0.0522 nm and a skewness of 3.05. This means that the data is not centered and the concentration of data is on the left of the mean value of 0.132nm. The mean roughness of this data (Ra), the average of the absolute value of the surface deviations from the mean plan, is 0.0338 nm. The error margin is then estimated to be 0.104nm. The effective $d_{33}$ value can be estimated using this area of confidence to provide a general constant for this nanofabric sample.
Figure 43. PMF (A) amplitude (B) phase of PVDF nanofabric
The mean amplitude of the PVDF nanofabric and the equation below [105] were used to calculate the $d_{33}$ piezoelectric constant of the sample:

$$d_{33} = \frac{[\text{Amplitude \ [nm]}]}{[\text{microscope \ gain}] \times [\text{Applied \ voltage \ bias \ [V]}]}$$

$$= \frac{0.132 \pm 0.05 \times 10^{-9}}{1.8 \times (2444 \times 10 - 3)}$$

$$= [41.82 - 18.2] \frac{pm}{V} \quad 2.1$$

The microscopic gain and the applied voltage bias are experimental parameters. The microscopic gain was provided by the Bruker Company for the Bruker Atomic Force Microscope. The electrospun nanofabric has the capabilities and scalabilities of most PVDF thin films while being made from nanofibers. The calculated $d_{33}$ value for the PVDF nanofabric is promising in comparison to the maximum theoretical and experimental $d_{33}$ value reported [61] for conventionally electrospun PVDF, which is 25 pm/V. This value is higher for PVDF thin film, and as reported by Swallow et al. [66] thin film PVDF can have $d_{33}$ values as high as 33 pm/V. When the bias voltage was applied, the amplitude on the surface of a single fiber was much greater (~0.4 nm) than that of its vicinity. This suggests that an increase in the fiber density can increase the overall $d_{33}$ value of the nanofabric.

### 2.4.2 Atomic Force Microscopy

Atomic force microscopy (AFM) has been used to study the material properties of the PVDF nanofabric including the elastic modulus, adhesion and the physical topography of the fabric.

#### 2.4.2.1 AFM Sample Preparation

AFM analysis was conducted on an electrospun PVDF nanofabric with polymer solution of 15 wt% PVDF and 2 to 3 DMF to acetone ratio. The Solution was fed into the nozzle at 6 ml/hr at 20 kV applied voltage. The distance between the nozzle and the grounded collector was set at 7 cm. The electrospun nanofabric had a thickness of 109 μm while the fiber diameters range from 800 nm to 1.5 μm. Figure 45 is the AFM scan showing the topography of the sample with a scan size of 20 μm by 20 μm.
2.4.2.2 AFM Parameters

The Bruker AFM device was used to perform the AFM scan. The mode was changed to PeakForce QNM, which provides the sample height using PeakForce tapping and quantitative nano-mechanical properties. The MESP-RC probe was chosen since it can scan over the air holes and account for the softness of the PVDF sample without breaking. After calibration of the AFM setup the deflection sensitivity was measured to be 13.6 nm/V and the probe had a spring constant of 5.133 N/m.
2.4.2.3  AFM Results and Analysis

The AFM results include two very important characteristics of the fabricated nanofabric: the topography, showing the woven fibers and their diameter; and the elastic modulus of the nanofabric. Figure 45 is the topography of the nanofabric.

![AFM 3D image of 20μm by 20μm scan of the PVDF nanofabric](image)

Figure 45. AFM 3D image of 20μm by 20μm scan of the PVDF nanofabric

Figure 46 (A) shows the adhesion of the nanofabric which varies from 0 to 365 nN. The adhesion analysis needs to be studied further with other probe for better precision. Adhesion did not have an impact on the analysis for this thesis and so further investigation was not done on adhesion. Figure 46 (B) shows the DMT modulus (after Derjaguin, Muller and Toporov model [106]) analysis from Nanoscope. The DMT theory is a contact theory that applies when measuring using a probe with small curvature radius and high stiffness. In this case the probe radius is 35-50 nm and the stiffness is 5.133 N/m. Figure 47 is the Nanoscope roughness analysis panel of the modulus channel, showing the topography of the modulus on the surface of the nanofabric. As it can be seen in the top of the table the average elastic modulus of the 20 μm by 20 μm sample was found to be 156 MPa. The modulus of a single fiber is around 112 MPa with a standard deviation of 12 MPa. It is hard to generalize the elastic modulus due to the many errors that error when the probe goes over the gaps or slips. Finally, it was decided to use the average value of 156 MPa for the purposes of mechanical energy calculations considering the potential error in measurement.
Figure 46. Adhesion (A) and modulus (B) of the PVDF nanofabric sample from Nanoscope

Figure 47. DMT modulus roughness analysis of PVDF nanofabric
Chapter 3

3 EXPERIMENTAL TESTING AND DISCUSSION

The PVDF nanofabric is modeled as a charge generator in parallel to a capacitor and resistor. In order to optimize the power output, impedance matching is done with the load resistance. The impedance of the PVDF material, shown in Figure 48 as $R_p$ and $C_p$, was measured using a capacitance meter (Agilent 4288A) operating at 1 kHz in parallel mode. A few different samples were tested for impedance measurements to make sure the different samples fabricated have the relatively close resistance and capacitance, as seen in Table 4. The average resistance was about 899.2 MΩ and the average capacitance 5.68 pF. In the following sections two setups are introduced for the testing of the nanofabric.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Capacitance (pF)</th>
<th>Resistance (MΩ)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>5.68</td>
<td>903</td>
</tr>
<tr>
<td>2</td>
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<td>872</td>
</tr>
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<td>3</td>
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<td>5</td>
<td>5.6</td>
<td>960</td>
</tr>
<tr>
<td>Average</td>
<td>5.684</td>
<td>899.2</td>
</tr>
</tbody>
</table>

The first method strains the nanofabric perpendicular to the direction of the electrical poling whereas the second method applies a force in the same direction as the poling. The $d_{33}$ constant
of the nanofabric is responsible for the voltage output in method 2 and the $d_{31}$ piezoelectric constant is responsible for the voltage output of the first method.

### 3.1 Method 1: Cantilever Stretching

The setup for this method is shown in Figure 49, the PVDF nanofabric was placed on top of the cantilever (non-conductive) and electrodes were attached to the two ends. Figure 49 (B) includes some locations at which the electrodes where placed at during the testing process. Conductive silver epoxy (*MG Chemicals*) was used as electrodes. The loading force on the cantilever was exerted using an impulse hammer (*Dynapulse*), as seen in the right corner of Figure 49 (B). An oscilloscope was used to display the voltage output from the circuit while the hammer was exerting force on the cantilever. It is worth mentioning that the natural frequency of the cantilever is 30 Hz. The current and voltage output were measured across the load resistor and used to calculate the output power. The applied force stretches the PVDF nanofabric which results in a voltage output. The deflection of the beam and its intensity reflect on the voltage and current output of the nanofabric. Figure 50 demonstrated the result from the stretch and release of the nanofabric on the voltage and current output. As the strain is released (the beam is returning to the neutral position) the outputs experience negative peaks.

![Figure 49. Experimental setup of testing the nanofabrics (A) before applying force (B) while hammer is being pressed on the cantilever](image)
The test was performed on more than 30 samples to observe the electrical output. The typical maximum voltage output range from 15-45 mV and the current from 0.5-4 nA depending on the applied force to the cantilever. The electrical power of the sample, the product of voltage and current, was as high as 184 pW and averaged at 70 pW.

3.1.1 Strain Measurements

A strain gauge (*Tokyo Sokki Kenkyujo Co.*) was attached to the top surface of the cantilever beam with epoxy to measure the axial strain. The strain $\varepsilon$ occurring on a bending surface can be expressed by:
\[ \varepsilon = \frac{t}{2r} \]

Where \( t \) is thickness of the beam and \( r \) is the bending radius, as seen in Figure 51. Since the bending radius of the cantilever beam and the thickness of the beam (~2 mm) were both much greater than the thickness of the PVDF nanofabric (100-120 \( \mu \)m) and the adhesion of the PVDF to the beam was very high, the strain of the PVDF was approximated to be the same as the strain of the outer surface of the beam measured by the strain gauge.

**Figure 51. Strain on bending surface**

### 3.1.2 Validating Piezoelectric Response

To confirm that the voltage output of the nanofabric with this setup is primarily from the piezoelectric properties of the PVDF, the experiment was performed on non-polarized electrospun PVDF shown in Figure 31. This material was not poled and other characterization methods had proved that the material was not piezoelectric. Figure 52 shows the voltage output of the material under the same experimental setup as Figure 49. The output voltage looks more like noise with no visible peaks indicating this material is not piezoelectric.
3.1.3 Power Conversion

As previously defined in Chapter 1, the energy conversion efficiency can be found using:

\[
k^2 = \frac{W^e}{W^m}
\]

where \( k \) is the electromechanical coupling coefficient of the piezoelectric material. The electric energy, \( W^e \), is found by integrating the product of voltage output and current of the excited PVDF nanofabric over time. The electrical energy was as high as 98.5 pJ and 70.6 pJ on average. The elastic or mechanical energy is calculated by

\[
W^m = \frac{1}{2} AYL_0 s^2
\]

The voltage output measurements using the cantilever design were done on numerous samples. The thickness of the nanofabric was 100 μm and the fiber diameter within the samples range from 800 nm-1.5 μm and the average elastic modulus from the AFM was 156 MPa. The calculated elastic energy was then calculated to be 0.642 nJ. By analyzing more than 15 samples the average energy conversion efficiency was found to be as high as 15.3% with an average 11%. This value is much higher than the average efficiency of experimental piezoelectric PVDF thin
film (0.5%- 4%) [66] and commercial thin film (0.5-2.6%) tested under the same condition as Figure 49.

3.2 Method 2: Stroke and Release

The second experimental setup strained the PVDF nanofabric samples in the direction parallel to the poling direction. Consequently, the sample was expected to generate more power per area of PVDF since the voltage will be generated via the transverse ($d_{33}$) piezoelectric mode. This section will discuss the testing setup and two different methods of applying force onto the sample. For both methods, the PVDF nanofabric was placed between two layers of PET with conductive electrodes painted on them using silver paint (*Ted Pella Inc.*), see Appendix B.

3.2.1 Actuator Controlled Stroke

In order to test the samples in the direction parallel to the direction of their polarization, a force needs to be applied vertically onto the surface. To control the force and the frequency of the force application, a piezoelectric actuator (*Noliac NAC2012*) was used. A function generator (*Tektronix AFG3102*) controlled the actuator. The output voltage and applied force were measured using an oscilloscope (*Tektronix DPO3014*) and a load cell. The setup is shown in Figure 53 (A). Figure 53 (B) and (C) are magnified sections of the setup showing the sample and the piezoelectric stack actuator. The frequency of the piezoelectric actuator was controlled between 5-60 Hz to try to work within a range similar to the environment the nanofabric would be used in. The frequency of the applied force via the stack actuator controlled the output frequency. The amplitude of applied voltage to the actuator was kept at 20 V to achieve maximum stroke of the piezoelectric stack. The force applied onto the sample was measured using a load cell that was attached just above the actuator. Note that the sample is placed between the actuator and the load cell shown in Figure 53 (B). Impedance matching was done at each frequency to achieve maximum power output. The point of contact between the actuator and the force cell has the area of 0.12 cm² which was measured by applying ink on the surface of the load cell and stamping a white surface since it was not an even surface.
Figure 53. Testing setup for measuring the voltage and power output using a piezoelectric actuator.

With the periodic load applied at 35 Hz, the sample demonstrated a steady maximum voltage output of 300 mV, as seen in Figure 54. The maximum power output corresponding to the periodic load was 210 pW. Depending on the applied load and the frequency at which the load was being applied, the maximum voltage and power outputs varied, for example the power output at 15 Hz was 70 pW and 170 pW at 60 Hz. The voltage output is proportional to the applied force while the output frequency is identical to the applied force frequency. To better demonstrate the relationship between the compress/release action of the actuator and the voltage output, Figure 55 is a zoomed in snapshot of Figure 54. It can be seen that by the onset of the compression force there is discharge of positive charges, as the compression is ending and changing into a release action the voltage begins to descend. Finally, as the release action is ending and turning into another compression cycle, the voltage begins to rise.
Figure 54. Voltage output, power output and applied force as measured by the load cell when actuator is at 35Hz
Figure 54 shows the output voltage, the corresponding power output at the load resistance of 594 MΩ, and the applied force at 35 Hz. The impedance of the PVDF nanofabric changed with frequency and the right axis of Figure 56 shows the impedance matching at each frequency. The correlation between the power output and the frequency is graphed in Figure 56. It can be easily observed that the curve reaches a peak near 35 Hz and starts to descend as the frequency increases. The highest power output of $2200 \text{ pw cm}^2$ occurs at the frequency of 35 Hz. The relationship between the applied force and the power output of the sample, in the case of using the actuator to apply a constant strain rate, can be used to predict the output of the sample under a certain pressure. For the case of the actuator applying a force at 35 Hz, the relationship is
17.32 \( \frac{\text{pW}}{\text{N.cm}^2} \). This means at this frequency for every Newton applied there will be 17.32 pW generated per cm\(^2\) of PVDF nanofabric.

Figure 56. Relationship between frequency and output energy and power per area of PVDF nanofabric

3.2.2 Impulse Stroke

In this method, an impulse hammer (Dynapulse) was used to apply force onto the surface of the sample. The applied force and piezoelectric voltage output were measured using the same oscilloscope (as previously seen Figure 53). Instead of using a controlled actuator to apply the force, the impulse hammer was used to monitor the voltage output of the material if hit with inconsistent forces. The power was calculated by measuring the current flowing through the circuit (Figure 48) when the load resistance was kept at 1 G\(\Omega\). Figure 57 is a picture taken while
running the experiments using the hammer. The tip of the hammer in contact with the sample has a diameter of 0.5 cm and so the contact area between the hammer and the sample is less than 0.78 cm². The maximum power output of the PVDF nanofabric per applied force is 32.01 \( \frac{\text{pW}}{\text{N.cm}^2} \). This value is almost twice the calculated value for the relationship between applied force and power output when the nanofabric was tested under the actuator controlled strokes. The discrepancy can be caused by two factors. The first factor is the samples used; the hammer test was done before the actuator controlled test and used another nanofabric. The second reason can be the load resistor; for the hammer test, the load was 1 GΩ whereas for the 35 Hz actuator controlled setup the load was 594 MΩ. Further investigation is needed to verify the reasons for this discrepancy.

![Figure 57. Testing the PVDF nanofabric using an impulse hammer](image)

The hammer test is intended for situations at which the nanofabric is placed in environments where the frequency of the input force is not controlled. Rather than constant applied forces, the sample is compressed with relatively different applied forces. The results seen in Figure 58 are for when the hammer hits the samples at random frequencies. The results agree with the findings from the previous testing setup and validate the piezoelectricity of the PVDF nanofabric.
Figure 58. Voltage output, power output and applied force as measured by the load cell placed inside the hammer for the PVDF nanofiber.
3.2.3 Validating the piezoelectric response

To insure the voltage output from the actuator controlled test is primarily due to the piezoelectricity of the PVDF nanofabric, a layer of PET is tested under the same testing setup shown in Figure 53. The voltage output is shown below in Figure 59. It is clearly observed that the applied force did not cause a voltage output from the material.

Figure 59. Voltage output and Applied force on PET sample
Chapter 4

4 SUMMARY AND FUTURE WORK

4.1 Summary of Contribution

After a thorough study of past research and developments in the field of energy harvesting using nanogenerators, a novel concept of a PVDF nanofabric was proposed. Detailed experimental analysis on material selection for electrospinning was done in order to conclude on the precise measurements of PVDF and solvents. Utilizing the theoretical fundamentals of electrospinning, different fabrication methods were tested to arrive at the final method of producing the PVDF nanofabric. Using a grounded drum setup to collect the electrospun PVDF nanofibers, the other parameters that could enhance the performance of the nanofabric were studied. Characterization methods, Piezoresponse Force Microscopy in particular, were crucial in determining the properties of the fabricated samples. The $d_{33}$ constant of the PVDF nanofabric was determined to be between 41.82 pm/V and 18.2 pm/V using PFM, and the elastic modulus of a single nanofiber was found, with AFM, to be 112 ± 12 MPa.

Two different testing methods were used to measure the power output of the nanofabric. The first method, stretched the nanofabric in the direction perpendicular to the electrical poling direction of the fibers, and the second applied a force in the direction parallel to the poling direction of the fibers. As expected the power output in the latter method was significantly higher than the first. Operating at its resonant frequency of 35 Hz the PVDF nanofabric had a power output of 2200 $\frac{pW}{cm^2}$ with 128 N of applied force. This value surpasses the output of any past research done in the field.

Liu et al. [107] present a similar approach to that of method 2 in section 3.2 of this report in which the grounded collector is a cylinder. Instead of using metal, the cylinder is made of glass with a copper interior, as seen in Figure 60. The solution used for electrospinning was a mixture of 18 wt% PVDF with Dimethyl sulfoxide (DMSO) and acetone. It was electrospun with an applied voltage of 18kV while the collecting tube had a rotation speed of 1900 rpm. The measured peak voltage with an applied load at 7 Hz, across a 10MΩ load resistor, was 76 mV. The measured current was 39 nA with maximum power at 577.6 $\frac{pW}{cm^2}$. 
4.2 Future Work

Recommendations for improving on the performance of the PVDF nanofabric can be divided into three sections: the first is optimizing the density; the second recommendation is on improving the testing setup; and finally utilizing the generated energy from the harvester.

The resonant frequency of the nanofabric needs to be reduced to around 5Hz in order to provide maximum power output when worn on as a patch. Increasing the nanofabric stiffness and density can do this. But as noticed during the characterization of the nanofabric, an increase in the density has a direct impact on the $d_{33}$ value. To make a better decision on how to reduce the resonant frequency, the connection between the nanofiber density, the resonant frequency and the piezoelectric constant needs to be studied further.

In order to test the samples in the most realistic way; a setup needs to be designed that strains the sample in both the parallel and perpendicular directions with respect to the poling direction. Finally, in order to integrate the energy harvester into wearable electronic devices, a circuit needs to be designed with capacitors to store the energy. Sohn et al. [74] have designed an electronic circuit with capacitors that can be used as an inspiration for a novel design.
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Figure 61A. Engineering Drawing of parallel electrode design
Figure 62A. Silver painted electrodes on PET sheets
APPENDIX C

Derivation of Equation 2.6:

Elastic Strain energy stored in a material being strained:

\[ \text{Elastic (mechanical) energy stored per Volume} = \frac{1}{2} S \cdot T \left[ \frac{J}{m^3} \right] \]

\[ \text{Elastic Energy} = \frac{1}{2} S \cdot T \cdot V = \frac{1}{2} V \cdot \frac{T^2}{Y} = \frac{1}{2} Y \cdot S^2 \cdot V = \frac{1}{2} Y \cdot S^2 \cdot A \cdot L_o \]

Where S and T are strain and Stress respectively, V is volume and Y is the elastic modulus. A is the cross sectional area and \( L_o \) is the effected length.

This equation can be used for calculating the mechanical energy stored when a piezoelectric material is working at low frequencies. The elastic (mechanical) stored energy is represented by the material’s maximum strain or stress [61].